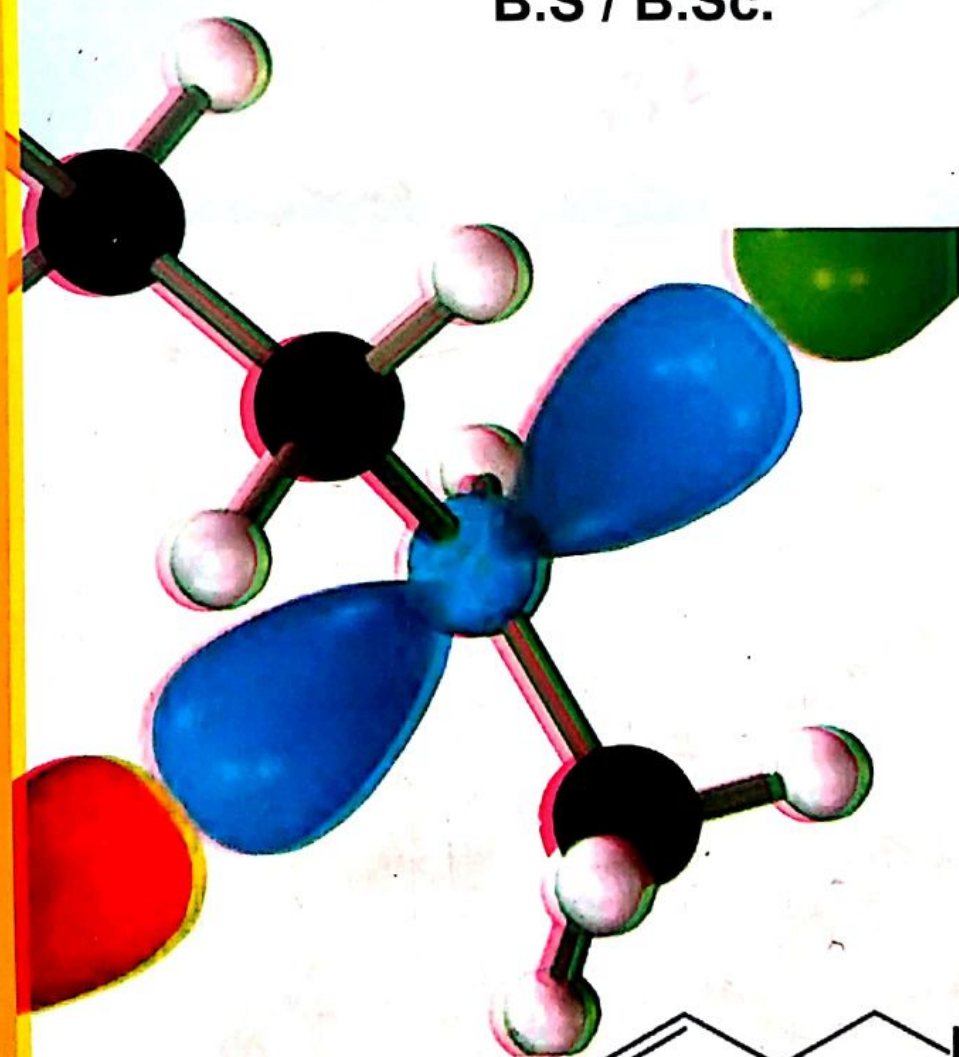
A Text Book of

Organic Chemistry

B.S / B.Sc.

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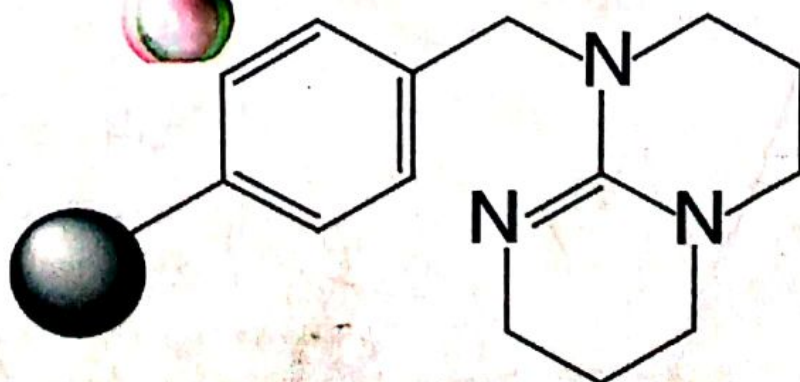
1. Chromatography and Spectroscopy

1.1 Introduction:

Chromatography (*Greek. Chroma, colour; Graphe, writing*) *is a technique for the separation of mixture of solutes brought about by the dynamic partition or distribution of dissolved or dispersed materials between two immiscible phases, one of which is moving past the other.* As the name suggests, this technique was originally confined to the separation of coloured substances, such as plant pigments or dyestuffs. Now the technique is equally well applied to colourless substances.

Definitions of Chromatography

Chromatography can be defined in various ways. Some common definitions of chromatography are:

1. *Chromatography is any process which is run in a column using a fixed bed.*
2. *Chromatography is the name given to the technique for the separation of a mixture of solutes brought about by the dynamic partition or distribution of dissolved materials between two immiscible phases one of which is moving past the other.*
3. ***Strain** has defined chromatography as any analytical technique for resolution of solutes, in which separation is made by differential migration in a porous medium and the migration is caused by flow of solvent.*
4. *According to **Williams and Weil** the chromatography is a process which allows the resolution of mixtures by effecting separation of some or all of their components in concentration zones on or in phases different from those in which they are originally present, irrespective of the nature of force or forces causing the substance to move from one phase to another.*
5. ***Michuel Tswett** has defined chromatography as a process used in separating substances by filtering their solution through a column of a finely powdered absorbent and then developing the column with a solvent.*
6. *According to **Cassidy,** chromatography is a separation process applicable to essentially molecular mixtures, in which the distribution of mixture occurs between an essentially two dimensional phases (or a thin phase and one or more bulk phases) which are brought into contact in a differential counter current manner.*

1.2 Classification of Chromatography

The most convenient classification of chromatography is based on the phenomenon involving the process of either partition or adsorption ; it has been classified in either of the two forms:

(i) Partition chromatography (ii) adsorption chromatography

(i) Partition chromatography *is a technique in which mixtures of substances are separated by means of partition between a moving solvent and a stationary liquid*

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which is held on a suitable solid support. When the solvent (moving phase) is a liquid it is called **liquid–liquid chromatography**, when it is a gas the technique is known as **vapour** or **gas-liquid chromatography**. The liquid-liquid separations are carried out on cellulose or moist silica gel, which may be in the form of thin sheets (*paper chromatography, PC*), thin layer (*thin layer chromatography, TLC*) or packed into columns (partition column chromatography). The medium in each case acts as a support for water. The most useful application of liquid-liquid chromatography is in the separation of water soluble substances.

(ii) Adsorption chromatography is a technique in which small differences in the adsorption behaviour of substances between a moving solvent (liquid or gas) and a stationary solid phase are utilized to achieve the separation. When the moving phase is a liquid, it is called **liquid-solid chromatography** or **adsorption column chromatography;** when the moving phase is a gas it is called **gas-solid chromatography (GSC)**.

1.3 Paper Chromatography

Paper chromatography is considered to be the simplest and most widely used of the chromatographic techniques because of its applicability to isolation, identification and, on occasion, quantitative determination of all low molecular mass organic and many inorganic compounds.

In paper chromatography separation of a mixture of substances is mainly done by the flow of solvents on a specially designed filter paper, called Whatman chromatographic filter paper. The stationary phase is the water present in the cellulose of the filter paper and the mobile phase is an organic solvent which is either immiscible or partially miscible with the stationary phase. The mobile phase (organic solvent) rises by the capillary action and by adsorption on the filter paper, the separation is effected by the differential migration of the mixture of substances. This occurs due to the differences in partition coefficients.

Types of Paper chromatography

Paper chromatography can be divided into two classes:

(a) Paper Partition chromatography. In this technique chromatographic filter paper acts as an inert support in which one solvent (usually water present in the cellulose of the filter paper) acts as a stationary phase and the other solvent (usually an organic solvent) acts as a mobile phase. Thus, the substances in a mixture move in two non-mixing solvents and partition between them.

(b) Adsorption paper chromatography. In adsorption paper chromatography the filter paper is impregnated with an adsorbent such as alumina or silica and a single solvent is allowed to flow over the unknown components. Thus, some of the components may be adsorbed more strongly than the others causing in the variation in the amount of the substance which tends to flow with the solvent. This causes the separation of the components

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Theory of paper chromatography

Paper chromatography can be considered to be a type of partition chromatography in which the mobile phase is an organic solvent and the stationary phase is water absorbed on the hydrophilic surface of the paper. Alternatively, the paper may be impregnated with anhydrous silica, alumina or ion exchange resin, here partition occurs as a consequence of solid-liquid or ion-exchange equilibria.

Two types of forces operate when a drop of solution is applied on the filter paper and treated with a solvent.

1. The Propelling force which tries to drag the substances in the direction of the flow of the solvent. This then depends upon (i) the rate of the solvent flow and (ii) the solubility of the substances in the solvent. Substances have different solubilities in different solvents and the solubility is affected by temperature. Sometimes the desired separation is not achieved with a single solvent; in such a case more than one solvents are used. This method is then called *two dimensional chromatography.*

2. The other force is the **retarding force,** which tries to drag the substance behind toward its point of application. This retardation depends on the adsorption and partition. The mechanism of separation in paper chromatography is largely partition in type; adsorption process plays only a small part. Because of the adsorptive nature of the filter paper (e.g; due to the presence of small quantities of carboxyl groups in the paper), some of the components in a mixture may be adsorbed strongly than the others causing variation in the amount of the substance which tends to flow with the solvent. Thus, when a drop of the solute is treated with the solvent on the strip of paper, the more strongly adsorbed component remains at the point of application while the less strongly adsorbed component will move along the paper with the solvent.

The process of partition is also operative on the paper. The cellulose of the filter paper always contains a small amount of water. Thus the substance on the filter paper moves in two non-mixing solvents (water of the paper and the organic solvent) and partition between them; the amount of solute in each solvent will naturally depend on the relative solubility of the substances in the two solvents.

R_f value. The relative rate of the movement of solvent and solute in paper chromatography is expressed by a term **R_f value** and is defined **as the ratio of the distance travelled by the compound at its point of maximum concentration to the distance travelled by the solvent.** Both the distances are measured from the point of application of the sample. **R_f value has no unit.**

$$R_f = \frac{\text{Distance moved by the sample}}{\text{Distance moved by the solvent}} = \frac{A}{B}$$

In many cases it has been observed that the solvent front is run off the end of the paper; it is therefore more convenient to use another term **R_x value** which is the **ratio of the distance travelled by a substance to the distance travelled by a chemically similar standard substance.**

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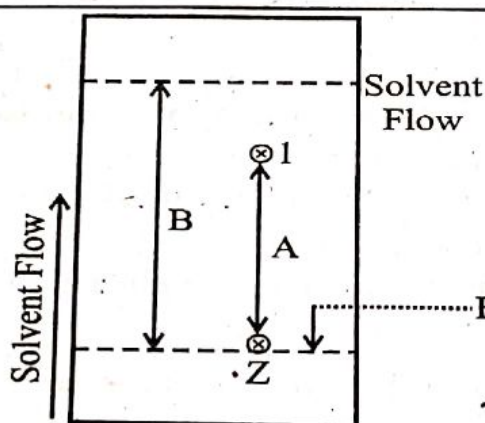
Fig. 1.1. Meausrement of R_f value
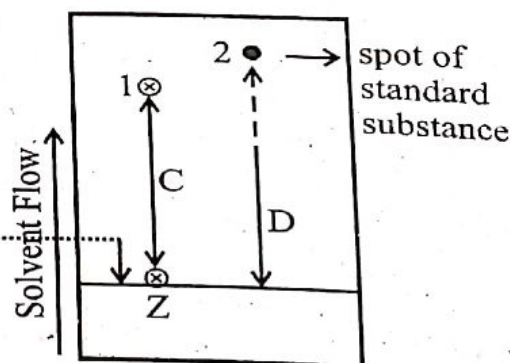
Fig.1.2. Meausrement of R_x value

$$R_x = \frac{\text{Distance moved by the substance}}{\text{Distance moved by the standard subtance, } x} = \frac{C}{D}$$

R_f values are different for different compounds. Every compound has different R_f value. Hence an unknown compound can be identified by comparing its R_f value with the literature value. Since R_f values differ with the solvent used, it is customary to quote the R_f value of a particular compound with reference to the solvent used. R_f value is always less than unity.

R_f values are affected by the following factors

(i) the temperature (ii) the quality of the paper (iii) the solvent used (iv) techniques employed (v) chemical reactions between the substances (vi) the distance travelled by the solute and solvent. (vii) pH of the solution (viii) the concentration of the separated substances.

1.4 Technique

The various operations involved in paper chromatography are:

(i) Choice of Filter Paper. The choice of filter paper depends on the (i) thickness (ii) flow rate (iii) purity and (iv) net strength of the filter paper. Generally Whatman filter papers are extensively used in paper chromatography.

(ii) Preparation of the solution. Pure solutions can be applied direct on the filter paper ; but solids are always dissolved in small quantity of a suitable solvent. Biological tissues are treated with suitable solvent and their extracts obtained. Concentrated solutions are generally applied on the filter paper to avoid diffusion through the paper.

(iii) Application of the sample to the paper. After the selection of the filter paper, a pencil line is drawn about 5 cm from one end. Several crosses, depending on the number of samples to be analysed, at equal distances apart are marked with the pencil on the line. A drop of the concentrated solution of each sample is spotted from a capillary pipette on to the marked spots. Platinum loops can also be used for applying the solution on the filter paper. Minimum volume of the concentrated

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solution is applied on the paper in order to avoid diffusion through the paper which leads to poor separations; spot should be about 5 mm in diameter. The solvent is now allowed to evaporate; the spots are dried. Now the paper is ready for the development.

(iv) Choice of the solvent. The most commonly employed solvents are the polar solvents, but the final selection depends on the nature of the substance to be separated. Water miscible solvents such as furan, propanol etc. have been extensively used. Since adsorption effects play an important part in some separations, a single solvent such as water can be used for developing the chromatogram. If pure solvents do not give satisfactory separation, a mixture of solvents of suitable polarity may be tried ; the added solvent may either be acids, bases or complexing agents. In most cases a mixture of n-butanol, acetic acid and water has been used. But in place of n-butanol, some tertiary alcohol is preferred because of the tendency of n-butanol to form esters with organic acids. Three components systems are widely used in paper chromatography. Generally a solvent or solvent mixture which gives R_f value of 0.2–0.8 for the sample should be selected.

(v) Development of Chromatogram. The chromatogram can be developed either by:

(i) The ascending technique in which the solvent is allowed to travel up the paper.

(ii) The descending technique in which the solvent is allowed to travel down the paper.

(iii) Another method of developing the chromatogram is radial development in which the solvent is allowed to move on the paper through a wick cut out from the paper.

In the ascending technique the solvent is placed at the bottom of a tank and the paper is suspended from the top with the help of a clip in such a way that the lower end of the paper containing the spots is well above the solvent.

2. In the descending technique the solvent is placed at the top of the tank in a trough and the chromatogram is so hanged that the solvent flows down the paper. The atmosphere in the tank is saturated with the vapour of the solvent by placing a small amount of it at the bottom of the tank. In the descending technique the solvent moves down the paper by the pull of the gravitational force as well as by the capillary action. Since the rate of flow of the solvent is greater in this technique the chromatogram is developed in a comparatively shorter time. Since the solvent can be allowed to run off the paper under the influence of gravity, the separation can be improved by increasing the effective length of the paper.

Spots
Base line
Anti-siphon Rod
Paper Suspended in trough
Separated Edge to allow solvent to flow uniformly off the paper

Fig:1.3. Descending Technique for Developing chromatogram

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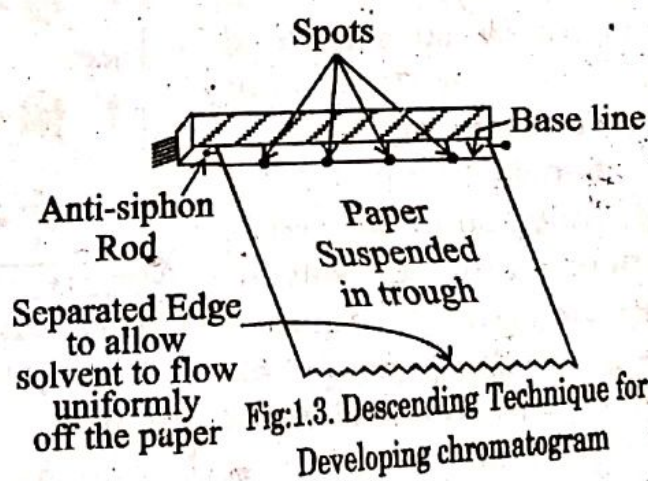
(iii) In the Radial or Disc Development a circular paper is marked with a pencil and a wick of about 2 cm is cut parallel to the radius from the edge to the centre. The sample solution is applied at the upper end of the wick in the centre. After drying the paper the wick is bent downwards at 90° to the plane of the paper, descending through an aperture in the glass plate into the solvent present in a petridish. The solvent flows through the wick to the sample spot and carries the solute with it, thus effecting separation of different components of a mixture.
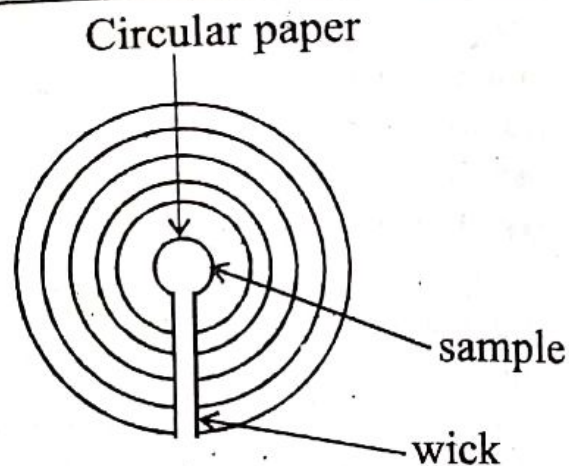
Fig:1.4 Raidal or Disc Technique

(vi) Drying the chromatogram: After the solvent has moved a certain distance for a certain time the chromatogram is taken out from the tank and the position of the solvent front is marked with a pencil. The chromatogram is now dried by blowing hot air from a hair dryer or by any other suitable method. After drying, the paper is ready for location of the compound.

(vii) Location of the Compound: The compounds on the chromatogram can be located either by physical methods, such as fluorescence, radioactivity, etc. or by chemical methods using chemical reagents to produce a distinctive coloured product. Coloured compounds are easily located on the paper and present no difficulty. They have to be located by either physical methods or chemical methods.

Separation Technique

In paper chromatography, a few drops of solution containing a mixture of the components to be separated is applied at a marked point about 2 cm above one end of a filter paper strip. After drying, that end of the paper is dipped into a solvent mixture consisting of aqueous and organic components; for example, water-butanol-acetic acid in 4 : 5 : 1 ratio, 77% aqueous ethanol or 1 : 6 : 3 water-n-propanol-conc. NH_4OH. The paper should also be in contact with the equilibrium vapours of the solvent. The solvent soaks into the paper by capillary action because of the fibrous nature of the solvent. The solvent migration direction can be arranged to be upwards (**ascending chromatography**) or downwards (**descending chromatography**). The aqueous (i.e, more polar) component of the solvent binds to the cellulose of the paper and there by forms a stationary phase

Fig. 1.5. Ascending paper chromatography

Fig. 1.6. Descending paper chromatography

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with it. The organic (non-polar) components of the solvent continue migrating, thus form the mobile phase.

The rates of migration of the various substances being separated are governed by their relative solubilities in the polar stationary phase and the non-polar mobile phase. In a single step of the separation process, a given solute is distributed between the mobile and stationary phase according to its **partition coefficient,** and equilibrium constant is defined as

$$K_P = \frac{\text{Concentration in stationary phase}}{\text{Concentration in mobile phase}}$$

The molecules are therefore separated according to their polarities, with non-polar molecules moving faster than polar ones.

After the solvent front has migrated an appropriate distance, the chromatogram (strip) is removed from the solution and dried. The separated materials, if not coloured may be visualized by spraying the chromatogram with a **reagent** solution that forms a coloured product upon reaction with the substance **under investigation.** For example, α-amino acids and primary amines react with **ninhydrin** to form an intensely purple compounds. The migration rate of the **substance may be expressed according to the ratio**

$$R_f = \frac{\text{Distance travelled by substance}}{\text{Distance travelled by solvent front}}$$

For given solvent system and paper type, each substance has characteristic R_f value.

Paper chromatography can be used as a preparative technique for purifying small amounts of substances. A solution containing the substance of interest is applied in a line across the bottom of a sheet of filter chromatographed. The substance of interest is located on the chromatograms by applying an appropriate detection technique to a small strip that has been cut out from the chromatogram along the direction of solvent migration or according to its known R_f value. Finally, the band of purified substance is cut out and the purified substance recovered by eluting it from the paper with suitable solvent.

For **two-dimensional paper chromatography,** sample is applied to one corner of a square sheet of filter paper and chromatographed in one solvent mixture. The sheet is then removed, dried, rotated 90° and is chromatographed parallel to the second edge using another solvent system. Since each compound migrates at a characteristic rate in a given solvent system, the second chromatographic step should greatly enhance the separation of the mixture into its components.
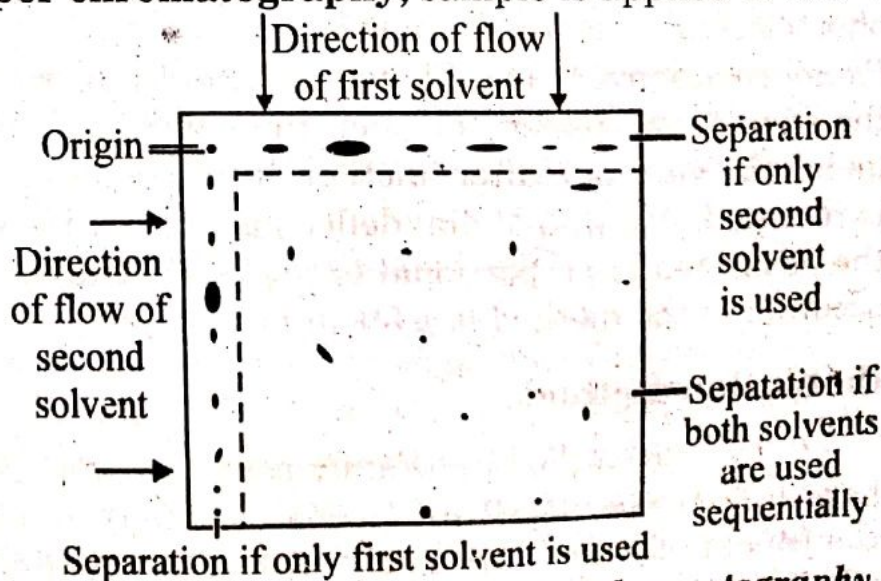
Fig.1.7. ***Two-dimensional paper chromatography.***

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(ii) Activation. Since water or other polar solvents affect the development by adsorption chromatography, they should be removed from the chromatoplates. This is known as activation. Adsorbents can be activated by placing the plates in an oven at 100-105°C for about 30 minutes. When plates are coated with cellulose or silica gel (for partition chromatography), the dry chromatoplates are exposed to the atmosphere for a time because a certain amount of moisture is essential for satisfactory resolution. This process is known as *deactivation*.

Ready-to-use thin layers, prepared with the most widely used adsorbents, are now available, e.g; as precoated glass plates and plastic foils. Plastic sheets precoated with cellulose are marked and are very convenient for inorganic TLC work as they can be cut to the required size.

(iii) Selection of solvent. A small amount of the sample is dissolved in a small amount of solvent such as benzene, ether or alcohol. The choice of solvent depends on two factors: one, the nature of the substances to be separated and the other, the nature of the adsorbent. The common procedure is to match the polarity of the solvent to that of the substances being separated. For polar substances such as alcohols, carboxylic acids and amines, the solution should be made in polar solvents and cellulose or silica gel layers are selected. Less polar substances should be dissolved in a suitable non-aqueous solvent and activated silica gel or alumina should be preferred as adsorbent. It has been observed that a combination of two solvents gives better separation than obtained with a single solvent.

(iv) Sample Application. Using a fine capillary tube or a micropipette the samples are applied in small spots to the base line about 2.5 cm from one edge of the plate and at least 1 cm apart. Not more than 1 cm^3 solution should be applied to each spot and the solvent is evaporated. The dry chromatoplate is now ready to be developed.

(v) Development of the chromatogram. The development of the chromatogram is usually carried out by **ascending technique** (in which the solvent moves from bottom to top direction) in a specially designed developing chamber, called tank. Since R_f values are affected by the degree of saturation of the atmosphere, it is, therefore, recommended that a paper impregnated with the solvent should be placed round the sides of the tank to ensure that the atmosphere in the tank is saturated with the solvent vapour. The chromatoplate is then placed between the glass plates and the trough is filled with the solvent. The tank is closed firmly with the lid.

After a certain time when the solvent has moved to about 10–12 cm above the origin, the plate is removed from the tank and the solvent front is carefully marked with a sharp pencil. The solvent evaporates very quickly from the plate. The plate is now ready for location of the compound.

Location of compounds of Chromatogram. Coloured substances can be seen directly and identified when viewed against the stationary phase while colourless species may usually be detected by spraying the plate with an appropriate reagent which produces coloured areas in the regions which they occupy.

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Many arom: tic and non-aromatic compounds appear as dark spots against a light background when the developed chromatogram is inspected under UV light of suitable wavelength in a darkened box.

Iodine is a very useful reagent which imparts a dark brown colour to the spots. Either a 10% methanolic solution of iodine are placed on the chromatogram or crystals of iodine are placed in the tank during the development. Iodine is a non destructive locating reagent and is very useful in identifying a large number of organic compounds.

Sulphuric acid is also a good locating reagent. But it is a corrosive reagent. It produces coloured compounds which are visible in day light as well as in UV light. H_2SO_4 mixed with oxidizing reagents such as $KMnO_4$, HNO_3, chromic acid, ceric sulphate etc. give better results.

A solution of the locating reagent of desired concentration is prepared and the plate is sprayed, dipped or streaked with this reagent, then heated for 5-30 minutes at 100-120°C

Detection, Estimation and identification

Quantitative analysis of separated constituents on thin layer plates is generally carried out by measurement of the photodensity and area of the spot, i.e; by photodensitometry of the plate.

An alternative procedure involves removal of the separated components from the plate by scrapping off the relavent portion of the adsorbent. The component is eluted (extracted) from the adsorbent with a suitable solvent and determined by an appropriate technique, e.g; by ultraviolet, visible or fluorescence spectrophotometry.

Thin Layer Chromatography (TLC) Technique

In thin layer chromatography, a sheet of glass of plastic plate is coated with a thin layer of adsorbent (cellulose, powder alumina, silica). This is done by mixing the adsorbent with a suitable liquid, usually water, to form a slurry. This is applied to the sheet of glass or plastic plate by spreading or dipping. After drying the plate a drop of mixture to be separated is placed just above one edge, which is then placed into a pool of solvent. The solvent is drawn up the adsorbent layer by capillary action. The separation of the sample mixture occurs into discrete spots. Partition TLC (PTLC) closely resembles ascending paper chromatography, and the same solvent systems and detection reagents are applicable.
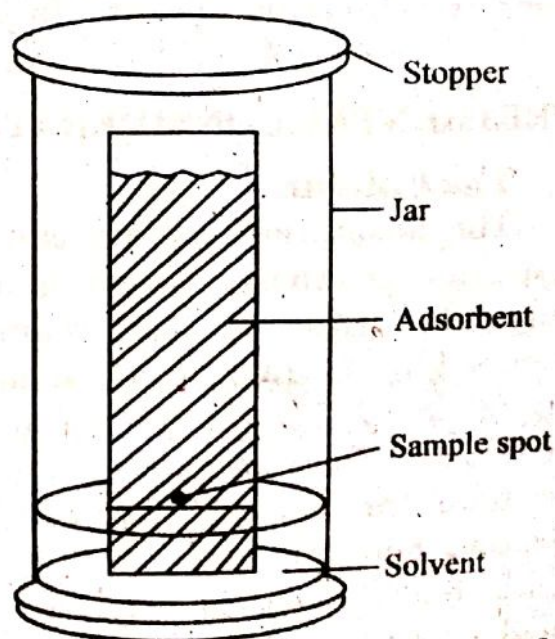
Fig.1.10 Thin layer chromatography

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APPLICATIONS OF TLC

Thin layer chromatography is being increasingly used for qualitative, quantitative and preparative analysis. The technique is extremely suited for analysis of trace components. A large number of organic and inorganic compounds have been separated and identified and whenever possible, quantitatively analysed. The interest in applying TLC is that the technique is very sensitive and gives sharper zones, hence better resolution. The continued progress in instrumentation to yield more accurate results will no doubt make the technique commonplace for quantitative analysis. The applications of TLC include the detection of by-products in synthetic processes, determination of the presence of impurity, removal of impurities and isolation of pure compounds, analysis of aminoacids, peptides, carbohydrates, lipids, steroids, bile acids, hormones, sterols, nucleosides, nucleotides, alkaloids, pesticides, insecticides, vitamins, pigments and inorganic anions and cations.

Quantitative analysis may be performed following elution or without removal of the layer, *i.e., in situ.* Both the techniques are widely used.

1.6 CLUMN CHROMATOGRAPHY

Column chromatography may be defined as a separation process involving the uniform percolation of a liquid solute through a column packed with finely divided material. The separation in the column is effected either by direct interaction between the solute components and surface of the stationary phase or by adsorption of solute by the stationary phase. Column chromatography involves adsorption, partition or ion-exchange phenomenon. In *adsorption column chromatography* the substances are preferentially adsorbed by adsorbent packed in the column, while in *paritition column chromatography* the separation of components of mixture distribute themselves in different ratios between two different solvents. In *partition column chromatography* the column is packed with silica gel or cellulose which contains significant amounts of water.

EXPERIMENTAL CONSIDERATIONS

1. The Column

The adsorption column can be of almost any size, shape, length or design, usually the size of the column is determined by the quantity of the mixture being fractioned. The column is commonly made of glass. The smaller the diameter of the column, the more effective will be the separation and the bands will be more distinct, but the passage of the liquids through it is necessarily slower than with the larger tube. For most purposes the
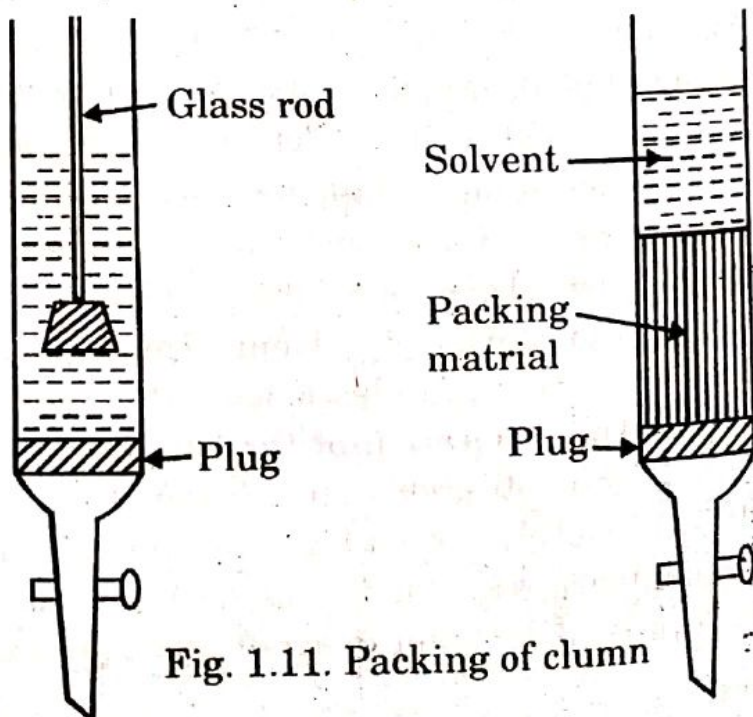
Fig. 1.11. Packing of clumn

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column recommended is 1 cm diameter, thin walled pyrex glass tube 15-20 cm long. One end of the tube is either drawn out or is closed with a rubber stopper.

Packing the column. Column is packed with dry powder, but wet packing is far more common and has certain advantages over dry packing.

(*i*) For *wet packing* the column is clamped in a vertical position and a thick slurry of the adsorbent in a suitable medium is poured through the open end gradually and allowed to settle under gravity until a column of the desired height is obtained. The tap at the lower end is then opened to allow the liquid to run out until it just covers the top of the medium.

(*ii*) In the *dry packing,* the dry powdered adsorbent is introduced through the open end, a good vacuum is applied on the bottom and the column is tapped with a light object, such as a pencil, until no more settling takes place. Ensure that the top is solid and unbroken.

2. Adsorbent

A large number of adsorbents are available which can be used in the column chromatagraphy, some being better for one use and some for other. In fact, no perfect adsorbent has been found.

Among the various adsorbents available two-alumina and magnesia-have been found to give satisfactory separations with most of the materials. Other adsorbents such as Na_2SO_4, $MgSO_4$, $Ca_3(PO_4)_2$, sucrose, starch, charcoal, $CaCO_3$ etc, have also been found useful for specific separations. In general alumina seems to have higher selective power and gives sharper and narrower bands. Sucrose and starch have proved to be very successful for the separation of chlorophylls.

Known, adsorbents have been classified into weak, strong and intermediate adsorbents depending upon their strength and other properties.

Weak adsorbents–Talc, sucrose, starch, insulin etc.

Intermediate adsorbents-Slaked lime, magnesia, $CaCO_3$, $Ca_3(PO_4)_2$ etc.

Strong adsorbents–Alumina, charcoal etc.

3. Solvents used with Columns

The separation in a column involves adsorption, partition and exchange phenomenon; the choice of solvent, therefore, depends on these properties.

Adsorption depends upon both the nature of the solvent and the adsorbent. In a chromatographic separation, it is likely that different solvents will be used for placing the solute on the column, developing the chromatogram and eluting the adsorbed materials. Generally a single solvent is used for all these operations, but in certain cases the simultaneous use of two or more solvents is advantageous. The purity of solvents is very important since impurities can alter the complete course of development. For better separations it has been found that the solution of the mixture should be prepared in a relatively non-polar solvent, development should be carried out with a somewhat polar solvent and even more polar solvent should be

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used for elution of the adsorbed materials. The increasing polarity of the common solvents is as follows:

Petroleum ether < carbon tetrachloride < cyclohexane < carbon disulphide < ether < acetone < benzene < ester of organic acids < chloroform < alcohols < water < pyridine < organic acids.

In separations involving partition column chromatography the solvents used are similar to those used in paper chromatography. In ion-exchange column chromatography the usual solvent is water and selective desorption of ions is carried out by altering the pH or concentration of ions in the eluting solvent.

4. Separation Techniques

The technique of column chromatography is much the same whether the separations are based on differential adsorption or on partition; the difference lies only in the packing material. In the partition chromatography procedure adsorbent powders are replaced by materials, such as silica gel or cellulose, which contain significant amount of water.

The technique of separation by column chromatography is very simple. A solution of the mixture to be separated is prepared in a relatively non-polar solvent and introduced into the column in a stepwise manner with the help of a pipette. The stopcock at the bottom is opened slightly to allow the solvent to run out until a small amount of the solution remains in the column covering the top of the packing material. More solution is then added and allowed to percolate through the column. When all the solution has been poured, the eluting solvent is then introduced and allowed to flow steadily through the medium. At first the components of the mixture are adsorbed at the top of the column and when the eluent percolates through the column, a process known as development occurs, which brings about the separation of the substance, and, if the components are coloured they impart diffused coloured zones in the column. As development continues, the separation becomes more and more pronounced.
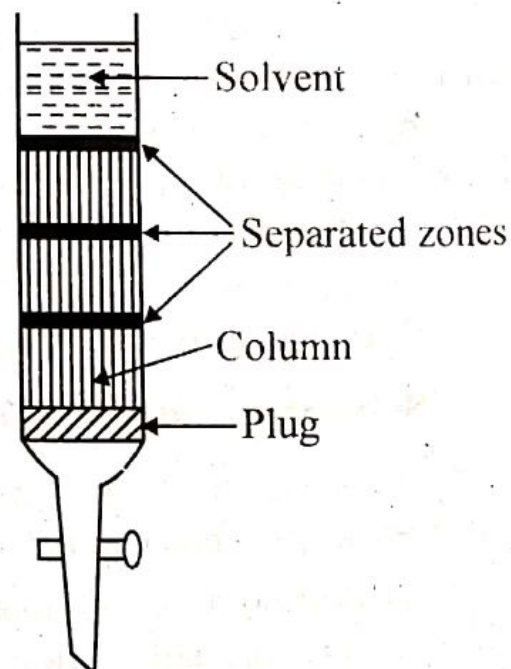
Fig.1.12 Separation of Mixture into zones

Examination and identification of compounds are relatively an easy matter in column chromatography. If the nature of the substance being separated is known, suitable solvents may be used to dissolve out the different zones and each fraction collected separately. Alternatively, the column is extracted, i.e., the adsorbent is pushed out of the column, eluting solvent is allowed to evaporate, each zone is cut

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with a knife and extracted in a suitable solvent. These fractions are then analysed by suitable method.

5. Identification of Compounds

Adsorption column chromatography is applicable not only to mixture of coloured substances, but even to mixtures of colourless substances. The identification of a coloured compound is relatively easier and present no difficulty. With colourless compounds the situation is, however, altogether different. In practice, a large number of fractions of eluate of equal volumes are collected and each fraction analysed separately by usual methods. Fractions containing no compound are rejected and those containing the compound are mixed and solvent evaporated to isolate the pure compound. But the procedure is time consuming and very tedious. It is, therefore, common practice in column chromatography to employ a fraction collector, which automatically collects equal volumes of the fraction in equal time.

Several physical or chemical methods may be applied for the identification of the separated compounds in different fractions. To examine a large number of fractions is again a formidable task.

Many colourless compounds fluoresce strongly in UV light. In continuous monitoring, the eluent is directly led into a device which measures the adsorbed UV light in the eluent and produces peaks on the graph. Thus, the fractions containing useful material can be readily located. This method is not suitable in cases where the compounds are affected by UV light, such as steroids and silver salts.

Chemical methods are used where it is not possible to identify the compound by the use of UV light or any other physical method. The fractions are treated with appropriate reagents to produce coloured products, e.g., vitamin A gives colour when treated with antimony chloride in chloroform.

Applications of Column Chromatography

The basic application of adsorption chromatography has been in the separation of the mixtures into the pure individual components. However, there are other applications of column chromatography; such as;

(1) the concentration of substance from dilute solutions such as those obtained when natural products are extracted with large volumes of the solvents from the leaves of plants, trees, roots or barks.

(2) removal of impurities in the purification of compounds.

(3) identification of unknown compounds and comparison of compounds thought to be identical;

(4) the determination of the homogeneity of chemical substances; and

(5) apart from those mentioned above. the greatest application of column chromatography has been in the separation and identification of inorganic anions and cations.

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Spectroscopy

1.7 Introduction

The branch of science which describes the interactions of electromagnetic radiation with matter is known as **spectroscopy.** *Spectroscopy may be defined as an area of study that probes molecular structure with electromagnetic radiation.* The absorption of electromagnetic radiation by a molecule as a result of the interaction of the radiation with the molecule gives very valueable information regarding the structure of the molecule.

Electromagnetic radiation is a form of energy, commonly known as *radiant energy.* Light is a form of electromagnetic radiation. According to quantum mechanics, electromagnetic radiation has the properties of both a wave and a particle-like discrete packets of energy, called **quanta** or **photons.** An electromagnetic radiation can be characterised in different ways using different parameters as described below.

Wavelength, λ. The distance between two successive crests or troughs of a wave in a beam of electromagnetic radiation is called *wavelength* and is denoted by λ (lambda). The units commonly used for wavelength are angstrom, nanometer, micrometer and meter (1m = 10^6 μm = 10^9 nm = 10^{10} Å)

Frequency, υ. The number of waves passing through a point on the path of a beam of radiation per second is called *frequency* and is denoted by *υ (nu).* It is expressed in *hertz (*Hz) or cycles per second (cps); (1 Hz = 1 cps).

Wave number, $\bar{\upsilon}$ is the number of waves passing per centimeter. A common unit for $\bar{\upsilon}$ is the *reciprocal centimeter,* cm^{-1}, ($1\, cm^{-1} = 100\, m^{-1}$). $\bar{\upsilon} = 1/\lambda$.

The **speed, c** of a wave is the distance through which a particular wave travels in one second and is denoted by c. Speed is related to frequency and wavelength by the expression;

$$c = \upsilon\lambda \quad or \quad \upsilon = \frac{c}{\lambda} \qquad \text{-----(1)}$$

Energy, E. Electromagnetic radiation can be characterized in terms of energy possessed by each photon of radiation. The SI unit for energy is Joule (J). Each photon has an energy which is proportional to the frequency of light.

$$E_{Photon} = h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon} \qquad \text{-----(2)}$$

where *h* is the Planck's constant having a value 6.625 × 10^{34} Js and c is the velocity of light which is 3.0 × 10^8 m/s.

Cosmic rays, gamma rays, X-rays, ultraviolet, visible light, infrared rays, micro waves and radio waves, all are electromagnetic radiation. Electromagnetic spectrum covers a wide range of wavelengths and the radiations of different wavelengths have different characteristics. The whole electromagnetic spectrum can

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be conveniently divided into several regions, each region can be defined by the limits of any of the four parameters, *i.e.*, wavelength, frequency, wave number or energy. In organic chemistry, the important wavelength regions are the ultraviolet, visible and infrared.

Table 1.1 Ranges of electromagnetic radiations in spectral region

Spectral region	Wavelength	Frequency (Hz)	Wavenumber (cm^{-1})	Energy (J)
Cosmic rays	10^{-4} Å	3×10^{22}	10^{12}	2×10^{-11}
	10^{-3} Å	3×10^{21}	10^{11}	2×10^{-12}
Gamma rays	10^{-1} Å	3×10^{19}	10^{9}	2×10^{-14}
X-rays	100 Å (10 nm)	3×10^{16}	10^{6}	2×10^{-17}
Ultraviolet	400 nm	7.5×10^{14}	2.5×10^{4}	5×10^{-19}
Visible	800 nm (0.8 μm)	3.8×10^{14}	1.3×10^{4}	2.5×10^{-19}
Infrared	10^{3} μm	3×10^{11}	10	2×10^{-22}
Microwave	10^{6} μm(1m)	3×10^{8}	10^{-2}	2×10^{-25}
Radiowave	10^{3} m	3×10^{5}	10^{-5}	2×10^{-28}

Principle of Spectroscopy:-

All organic compounds interact with electromagnetic radiation, that is, they absorb energy. When a molecule absorb energy, a transformation occurs. Lower energy radiation may cause a molecular rotation, or a bond vibration. Higher energy radiation may cause the promotion of electrons to higher energy levels or bond cleavage.

Whether the transformation involves molecular rotation, bond vibration, or electronic transition, the molecule absorbs only the wavelength of radiation with exactly the energy necessary for the transition. The absorption of wavelengths of radiation is selective for a particular transition which depends on the structure of the molecule. By measuring the absorption spectra of known compounds we can correlate the wavelengths of energy absorbed with characteristic structural features. This information is then used to determine the structure of unknown compounds.

During absorption some of the molecules falling in the path of the incident beam, collide with photons of radiant energy. However, only those photons get absorbed whose energy exactly equals the difference in energy, ΔE between the ground and the excited states of the molecules.

$$\Delta E = h\upsilon = hc/\lambda$$

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Spectrophotometer. The instrument used to measure the amount of electromagnetic radiation absorbed by a compound is called **spectrophotometer** or **spectrometer.** It consists of light source of radiation, with a prism that can select the desired wavelengths which are passed through a sample of the compound being investigated. The radiation that is absorbed by the sample is detected and is recorded on a chart against the wavelength or wave number. Absorption peaks are plotted as *minima in infrared,* and usually as *maxima* in *ultraviolet* spectroscopy.
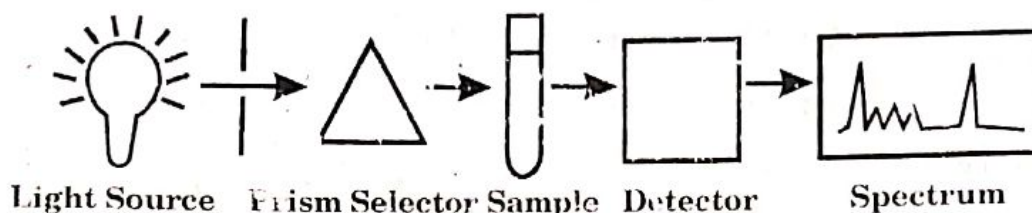
Fig. 1.13. Basic components of a spectrophotomer

Beer – Lambert Law. Electronic spectra of organic substances are most frequently recorded in solution and the Beer-Lambert Law expresses mathematically the relationship between the amount of light absorbed and (i) the concentration of the solution and (ii) the length of the solution through which light passes. Mathematically

$$A = \log \frac{I_0}{I} = \epsilon cl \qquad or \qquad \epsilon = A/cl$$

where I_0 is the intensity of the incident radiation, I is the intensity of the transmitted radiation, c is the concentration of absorbing compound in moles per dm^3, l is the length of sample tube in cm, A is called **absorbance** of the solution and ϵ is called **molar absorptivity** or **molar extinction coefficient.** Some instruments are calibrated in the units of absorbance. The ratio, I/I_0, is transmittance and $I/I_0 \times 100$ is per cent transmittance.

Concept of Max. Peaks in ultraviolet and visible spectra are often quite broad. That is, they span many wavelengths. It is convenient to specify the molar absorptivity (ϵ) at the wavelength of greatest intensity of absorption within a broad peak. That wavelength is given the symbol λ_{max}, and the molar absorption at this wavelength is ϵ_{max}. A spectrum may have several different maxima each with a characteristic value of ϵ_{max}. The value of λ_{max} is read directly from the spectrum, but the absorptivity ϵ is calculated from the concentration of the solution and the path length of the cell. For example, ϵ_{max} is calculated, for a compound whose maximum absorbance (A) is 1.2. The cell length (l) is 1.0 cm and the concentration is 7.6×10^{-4} M. Then

$$\epsilon = \frac{A}{cl} = \frac{1.2}{(7.6 \times 10^{-4})(1.0)} = 1.6 \times 10^{3}$$

The UV absorption spectrum of 2, 5-dimethyl – 2, 4 – hexadiene is shown in Fig. It shows a broad absorption band in the region 210 – 260 nm with a maximum

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at 241.5 nm. It is this wavelength of maximum absorption (λ_{max}) which is reported in chemical literature

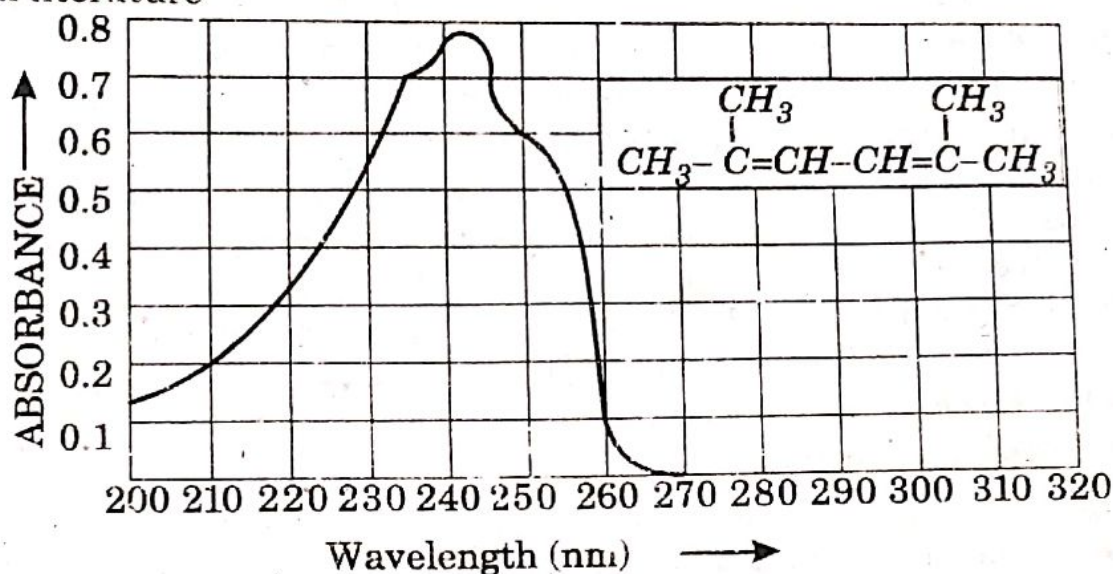



Fig. 1.14-UV absorption spectrum for 2, 5-dimethyl- 2, 4-hexadiene.

There are four spectroscopic methods which are widely used in organic chemistry. They are ultraviolet-visible, infrared, nuclear magnetic resonance and mass spectroscopy.

1.8 Ultraviolet–Visible Spectroscopy:-

In ultraviolet–visible spectroscopy, the absorption of ultraviolet (200–400 nm) and visible (400–750 nm) radiation by molecules is associated with the excitation of loosely held electrons (such as unshared electrons or electrons in a π bond) from a lower-energy, occupied molecular orbital (MO) to a higher energy, unoccupied molecular orbital (MO*).

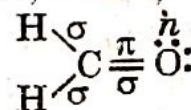
There are three kinds of electrons, those in σ bonds, those in π bonds, and unshared electrons which are denoted by the letter n for nonbonding, e.g;

On absorbing energy any of these electrons can enter excited states, which are either antibonding σ* or π*. All molecules have σ and σ* orbitals, but only those with π orbitals have π* orbitals. Only the n→π*, π → π*, and more rarely the n →σ* excitations occur in the near ultraviolet and visible regions, which are the available regions for ordinary spectro-photometers. The energy required for σ → σ* transition is very high and therefore, occurs in the vacuum UV region (below 200nm) which is not usually accessible in most UV–Vis spectrophotometers. The relative energy for 3 electronic transitions detectable by UV spectrophotometer in order of increasing ΔE is n → π* < π → π* < n → σ*. In fact, the absorption of UV–Vis radiation by a molecule results in the electronic transition from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO).

Fig.1.15 Relative energy changes involved in various electronic transitions

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Some of the most important electronic transition in organic compounds are:

1. $\sigma \rightarrow \sigma^*$ transition. This type of transition is generally observed in standard molecules without lone pair of electrons. Since the $\sigma \rightarrow \sigma^*$ transition involves a large energy change, the resulting band is observed in the ultra-violet region 125–135 nm. Methane and ethane show λ_{max} at 121.9 nm and 1350 A^o, respectively.

2. $n \rightarrow \sigma^*$ transition. In addition to $\sigma \rightarrow \sigma^*$ transition, the saturated compounds having lone pair (non-bonding) electrons undergo $n \rightarrow \sigma^*$ transition. This type of transition involves smaller energy change compared to $\sigma \rightarrow \sigma^*$ transition and, therefore, the corresponding band is observed in the range 180–200 nm (U.V.region). Methyl alcohol and methyl chloride absorb in this region. Trimethylamine and methyl iodide, however, absorb at slightly longer wavelengths, the λ_{max} being 227 nm and 2630 A^o, respectively.

3. $n \rightarrow \pi^*$ transition. Unsaturated compounds with unpaired electrons show this transition which corresponds to the weakest energy. All compounds having carbonyl group *e.g.*, formaldehyde, show this transition. The band corresponding to this transition is observed in the visible region, λ_{max} for acetone is 279 nm and that for nitromethane is 2740 A^o.

4. $\pi \rightarrow \pi^*$ transition. Both $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions occur in unsaturated hydrocarbons. The $\pi \rightarrow \pi^*$ transition is observed at about 180–190 nm, and 200–210 nm for aliphatic and simple aromatic compounds, respectively. For >C=O and –C≡N groups this transition is observed at 190 nm. In the solvents of high dielectric constant or of hydrogen bonding, *hypsochromic shift* (shift of wavelength towards shorter wavelength, also known as *blue shift*) has been observed for this transition. If an electron donating group is introduced then in the high dielectric solvents a *bathochromic shift* (*red shift i.e.,* shift towards higher wavelength) is observed. The $n \rightarrow \pi^*$ transition in the acidic medium often disappears either due to Protonation or due to formation of an adduct that ties up the lone pair, e.g., BCH_3^+, where B is the base molecule such as pyridine. The energy required for these transitions is in the order $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$.

Visible-ultraviolet spctrometers are used to measure the amount of light absorbed at each wavelength of the visible-ultraviolet region. In these spectrometers a beam of light is split; half the beam (the sample beam) is directed through a transparent cell containing a solution of the compound being analysed and half (the reference beam) is directed through an identical cell that contains only the solvent. Solvents are chosen to be transparent in the region being analysed. The detector continuously measures the intensity ratio of the reference beam (I_r) compared with the sample beam (I_s). As the spectrometer scans the wavelengths in this region, a chart recorder draws a graph (spectrum) of the absorbance of the sample as a function of the wavelength. The absorbance, A, of the sample at a particular wavelength is defined by the equation (Beer's law):

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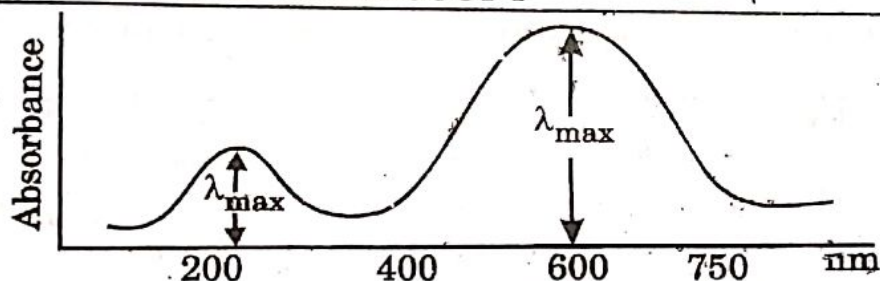
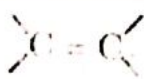
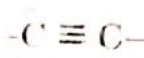
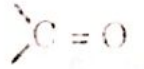
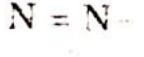


Fig. 1.16. A sample UV-Vis spectrum

The chromophore. Any functional group in a molecule, such as the carbonyl group in aldehydes and ketones and double bond in alkenes, which is responsible for the absorption of electromagnetic radiation in the UV-Vis region is called **chromophore.** The chromophores generally contain some degree of unsaturation. Besides chromophoric groups, there are certain functional groups, such as NH_2, OH etc. which are not chromophores themselves but when attached to a given chromophoric system, usually cause the absorption of the chromophore to shift to a longer wavelength. For example, substitution of alkoxy groups on C = C (e.g., methyl vinyl ether , $CH_2 = CHOCH_3$) causes a shift to longer wavelength **(red shift).** Such functional groups (alkoxy in the above example) are called **auxochromes.** All **auxochromic** groups contain nonbonding electrons which are in conjugation with the chromophore. This conjugation shifts the λ_{max} to a longer wavelength. The conjugation of an auxochrome with a chromophore shifts the $\pi \rightarrow \pi^*$ absorption to a longer wavelength. The shift of the λ_{max} to a longer wavelength is called **red shift** or **bathochromic shift.** A shift of the λ_{max} to a shorter wavelength is called **blue shift** or **hypsochromic shift.**

Chromophores: Groups that cause light to be absorbed are called chromophores.

Auxochrome. Groups that do not in themselves show selective absorption above 200nm but which when attached to a given chromophoric system, usually cause a shift in the absorption to longer wavelength and an increased intensity of the absorption peak. These are called auxochromic groups. All auxochromic groups contain nonbonding electrons which are in conjugation with the chromophore.

Bathochromic shift (Red Shift). It is a shift of λ_{max} to longer wavelength.

Hypsochromic Shift (blue shift). It is a shift of λ_{max} to shorter wavelengths.

Hyperchormic shift. It is accompanied by increase in intensity of absorption.

Hypochormic shift. It is accompanied by decrease in intensity of absorption.

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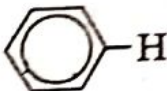
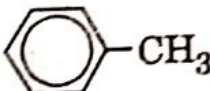
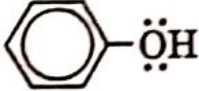
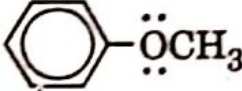
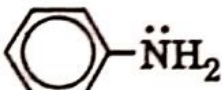
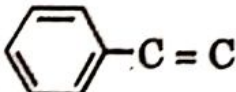
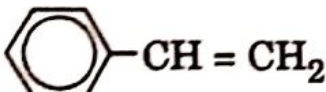
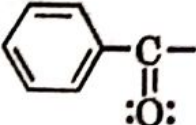
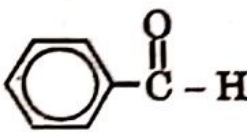
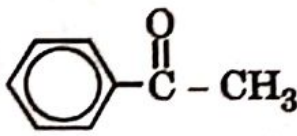
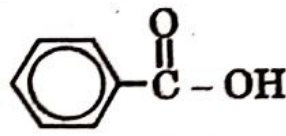
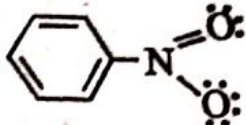
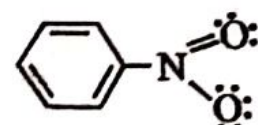
Table. 1.2 Ultraviolet absorptions of some simple isolated chromophores

Chromophore	Example	λ_{max}(nm)	Electronic Transition
>C = C<	Ethylene	171	$\pi \longrightarrow \pi^*$
–C ≡ C–	Acetylene	173	$\pi \longrightarrow \pi^*$
>C = O	Acetone	190	$\pi \longrightarrow \pi^*$
		280	$n \longrightarrow \pi^*$
–C ≡ N	Acetonitrile	167	$\pi \longrightarrow \pi^*$
N = N	Azomethane	338	$n \longrightarrow \pi^*$
(benzene ring)	Benzene	254	$\pi \longrightarrow \pi^*$

Conjugated Systems. Conjugation of π bonds (a chromophore in conjugation with another chromophore) causes molecules to absorb at longer wavelengths. As the number of conjugated π bonds increases, λ_{max} increases. Cyclic polyenes absorb at higher wavelengths than do acyclic polyenes. For example, it is seen that ethylene absorbs at 171 nm, 1, 3–butadiene absorbs at 217 nm, 1, 3, 5–hexatriene absorbs at 274 nm and 1, 3–cyclohexadiene absorbs at 256 nm. Why λ_{max} for 1, 3–butadiene, **is higher than for ethylene?** This is because in 1, 3–butadiene, the π orbitals of the two ehtylenic bonds combine to form four new π molecular orbitals – two bonding (π_1 and π_2) and two antibonding (π_3^* and π_4^*), all having different energy (see MO theory). For 1,3–butadiene, the electronic transition (excitation) is from π_2, the highest occupied MO (HOMO) to π_3^*, the lowest unoccupied MO (LUMO). The ΔE for this transition is less than the ΔE for $\pi \rightarrow \pi^*$ for ethylene. Therefore, λ_{max} for 1,3–butadiene is greater than λ_{max} for ethylene.

The same principle is applicable when unlike chromophores are in conjugation with each other as, e.g., in α, β unsaturated carbonyl compounds. Methyl vinyl ketone, $CH_2 = CHCOCH_3$, shows $\pi \rightarrow \pi^*$ absorption at 215 nm, while carbonyl group and isolated double bond both do not show $\pi \rightarrow \pi^*$ absorption above 200 nm.

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Table.1.3 Ultraviolet absorptions of conjugated chromophores (Aliphatic Compounds).

Chromophore	Example (s)	Absorption: Approximate Position λ_{max}(nm)	Approximate Intensity ϵ_{max}
C=C–C=C	$CH_2 = CH - CH = CH_2$	217	21,000
$(C = C)_n$	$CH_2 = CH - CH = CH - CH = CH_2$ ($n = 3$)	270	40,000
	$CH_2 = CH - (CH = CH)_2 - CH = CH_2$ ($n = 4$)	310	60,000
	$CH_2 = CH - (CH = CH)_4 - CH_2 = CH_2$ ($n = 6$)	380	150,000
	$CH_2 = CH - (CH = CH)_6 - CH = CH_2$ ($n = 8$)	415	200,000
$C = C - \overset{O}{\overset{\Vert}{C}} -$	$CH_2 = CH - \overset{O}{\overset{\Vert}{C}} - H$	218 320	18,000 30
	$CH_3(H)C = C(COOH)H$	206 242	13,500 250
	$CH_2 = CH - \overset{O}{\overset{\Vert}{C}} - CH_3$	213 320	7,000 30
$(C = C)_n - \overset{O}{\overset{\Vert}{C}} -$	$CH_3 - (CH = CH)_2 - \overset{O}{\overset{\Vert}{C}} - H$	270	27,000
	$CH_3 - (CH = CH)_4 - \overset{O}{\overset{\Vert}{C}} - H$	343	40,000
	$CH_3 - (CH = CH)_6 - \overset{O}{\overset{\Vert}{C}} - H$	393	63,000
	$CH_3 = (CH = CH)_7 - \overset{O}{\overset{\Vert}{C}} - H$	415	65,000

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Table.1.4. Ultraviolet absorptions of conjugated chromophores (Aromatic Comp unds).

Chromophore	Example (s)	Absorption: Approximate Position λ_{max}(nm)	Absorption: Approximate Intensity ϵ_{max}
Benzene	C_6H_5–H	184 203 255	47,000 7,000 230
	C_6H_5–CH_3	206 261	7,000 225
	C_6H_5–$\ddot{O}H$	211 270	6,000 15,000
	C_6H_5–$\ddot{O}CH_3$	217 269	6,400 1,500
	C_6H_5–$\ddot{N}H_2$	230 280	8,600 1,400
C_6H_5–C = C	C_6H_5–CH = CH_2	248 280	14,000 800
C_6H_5–C(=:Ö:)–	C_6H_5–C(=O) – H	250	11,400
	C_6H_5–C(=O) – CH_3	246	10,000
	C_6H_5–C(=O) – OH	230 272	11,600 950
C_6H_5–N(=Ö:)–Ö:	C_6H_5–N(=Ö:)–Ö:	270	7,800

The following points should be kept in mind while interpreting a UV–Vis spectrum.

1. Nonconjugated alkenes show an intense absorption below 200nm and is therefore inaccessible to most commonly used UV spectrometer. The absorption is caused by $\pi \rightarrow \pi^*$ transition.

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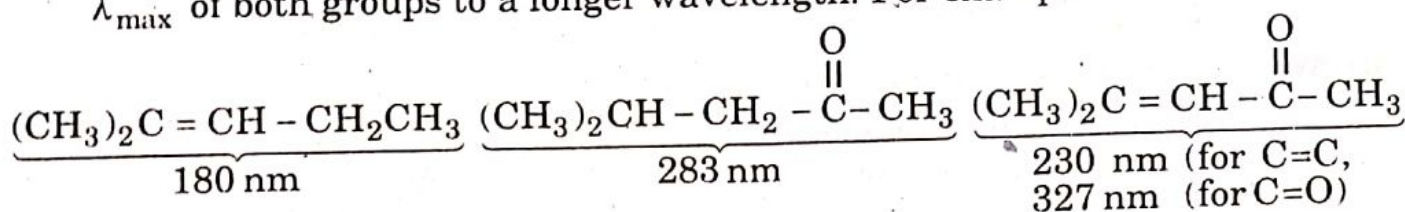
2. The carbonyl group of aldehydes and ketones shows two peaks. The absorption in the 180–190 nm region is caused by $\pi \rightarrow \pi^*$ transition and this is the more intense peak. The absorption in the 275–290 nm region is caused by $n \rightarrow \pi^*$ transition and shows a band of low intensity.
3. When a molecule contains two or more nonconjugated carbon–carbon double bonds, the UV spectrum is that expected of a simple alkene, e.g., 1,5–hexadiene (λ_{max} = 178nm). However, when the double bonds are conjugated, λ_{max} is shifted to longer wavelength, e.g., 2, 4–hexadiene (λ_{max} = 227 nm).
4. Conjugation of a carbon-carbon double bond and a carbonyl group shifts the λ_{max} of both groups to a longer wavelength. For example

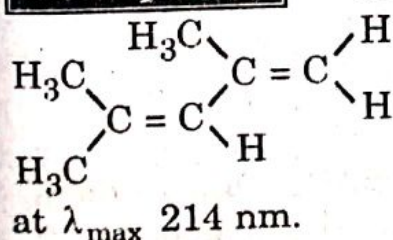
$$\underbrace{(CH_3)_2C=CH-CH_2CH_3}_{180\text{ nm}} \quad \underbrace{(CH_3)_2CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_3}_{283\text{ nm}} \quad \underbrace{(CH_3)_2C=CH-\overset{O}{\overset{\|}{C}}-CH_3}_{\substack{230\text{ nm (for C=C,}\\ 327\text{ nm (for C=O)}}}$$

5. As the number of double bonds in conjugation increase, λ_{max} also increases.

The Woodward-Fieser rules for absorption spectra of dienes. When alkenes are substituted by alkyl groups, generally a bathochromic (λ_{max} shifting to higher values) or hyperchromic shift (increase in intensity absorption) are produced. However, in certain cases of alkyl substitution, the wavelength increases but intensity of absorption decreases.

Cyclic dienes are of two types: (i) the Homoannular dienes (in which both the double bonds are present in the same cyclic ring); and (ii) Heteroanular dienes (in which the double bonds are present in different rings).

By studying a large variety of dienes of each type, Woodward and Fieser gave empirical rules to explain the UV spectra of dienes.

Table.1.5. Woodward-Fieser rules for dienes

Parent diene:	λ_{max}
Heteroannular and acyclic	214 nm
Homoannular	253 nm
Extended conjugation (per C = C)	+30 nm
Alkyl substituent (per group) or ring residue	+5 nm
Ecocyclic double bond	+5
Polar groups	
$-OCOCH_3$	0
$-OR$	+6
$-Cl$, $-Br$	+5
$-NH_2$	+60

Example 1. Apply Woodward - Fieser rules to calculate the λ_{max} for

$$(H_3C)_2C=C(CH_3)-CH=CH_2$$

[structure: H_3C, H_3C on C=C; H_3C and H on next carbon; C=C with H, H]

when the parent compound $H_2C=CH-CH=CH_2$ absorbs at λ_{max} 214 nm.

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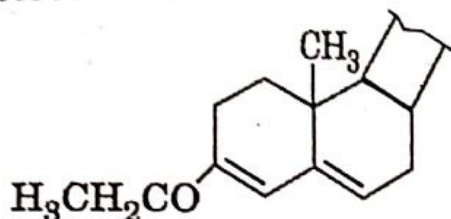
Solution: Parent absorption of the diene = 214 nm
Increment for 3 methyl groups = $3 \times 5 = 15$ nm
Expected λ_{max} = $214 + 15 = 229$ nm

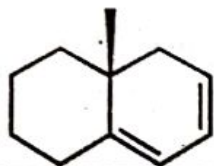
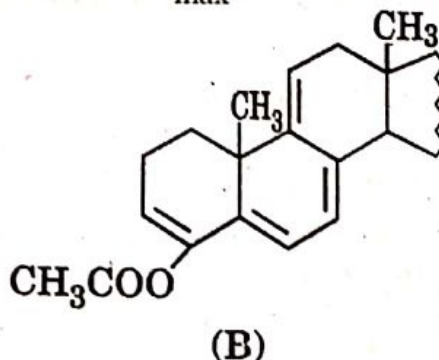
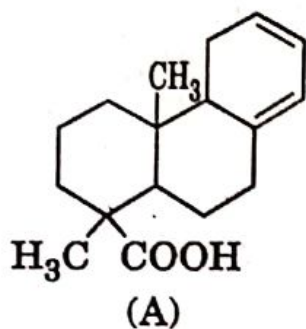
Example 2. Calculate the λ_{max} for the following compound when the trans-butadiene absorbs at 214 nm:

Solution.

Parent trans-diene absorption	= 214 nm
2 Ring residue and one methyl group	= $2 \times 5 + 5 = 15$nm
1 Ecocyclic double bond	= 5nm
–OR	= 6*nm*
Total	240 nm

The compound is expected to exhibit a λ_{max} at 240 nm.

Example 3. Calculate the λ_{max} value for the compound, when the parent diene has a λ_{max} at 253 nm.

Solution:

Parent diene homoannular	= 253 nm
Substituents	= 15 nm
Ecocyclic double bonds = 1×5	= 5 nm
Predicted λ_{max}	273 nm

Example 4. Calculate the λ_{max} value for the compound (B) given below. It has been observed that the parent cis diene (A) has a λ_{max} at 253 nm.

Solution:

In the parent cis diene (A) absorption is	= 253 nm
3 Ring residues + 2 methyl groups	= $5 \times 3 + 5 \times 2 = 25$
2 double bonds which extend conjugation	= $2 \times 30 = 60$ nm
3 Ecocyclic double bonds	= $3 \times 5 = 15$ nm
CH_3COO^-	= 0 nm
Total	= 353 nm

The compound (B) is expected to observe λ_{max} at 353 nm.

1.9 Infrared Spectroscopy

Wavelengths in IR region are usually measured in micrometers (μm), where $1\mu m = 10^{-6}$ m or 10^3 nm (formerly called a micron represented by the symbol μ). IR

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region extends from about 0.8 to 20 μm and most of the commercial IR spectrometers cover the region from about 2 to 17 μm.

Ordinary IR region extends from 2.5 to 16 μm (4000 to 625 cm^{-1}). The region extending from 0.8 to 2.5 μm (12, 500 to 4,000 cm^{-1}) is called the **near infrared region** whereas the one extending from 16 to 200 μm (625 to 50 cm^{-1}) is called the **far infrared region.**

IR spectra are commonly described in terms of the frequencies of radiations absorbed rather than their wavelengths. This is logical since frequency is directly proportional to the energy of radiation whereas wavelength is inversely proportional to energy. The most common unit used to describe IR spectra is the wave number, $\bar{\upsilon}$ which represents the number of vibrations of radiation per centimetre (cm^{-1}). Wavelengths in μm can be converted into wave numbers by the formula

$$\bar{\upsilon} = \frac{10^4}{\lambda} \qquad [\because 1\ \mu m = 10^{-6}\ m = 10^{-4}\ cm]$$

For IR spectra, the units employed are μm for wavelength (λ) and cm^{-1} for wave number ($\bar{\upsilon}$). Workers in respective fields have used both these units.

An infrared (IR) spectrometer subjects a compound to infrared radiation in the 4000–625 cm^{-1} range. Although this radiation is weak, it does supply sufficient energy for bonds in the molecule to vibrate. The molecular motion that is affected by the absorption of quanta of the infrared radiation is the **vibrational motion.** The studies of vibrational spectra of molecules lead to the information on the flexibility of the molecules *i.e.,* the ease with which the bond lengths and bond angles can be distorted from the values that they have in the equilibrium configuration of the molecule. The small displacement of the constituent atoms from their equilibrium positions can be seen in terms of vibrational motion of the atoms. Such changes in the bond-length produce a change in the dipole moment of a heteronuclear molecule and if the oscillating dipole couples with the electrical field of the radiation (of suitable frequency) an exchange of energy takes place.

Hooke's Law: A simple harmonic oscillator is the one in which the restoring force is proportional to the displacement in accordance with Hooke's law i.e.,

$$F = -k'x$$

For a diatomic molecule, $x = R - R_e$, where R is the distance to which the atoms have been stretched and R_e is the equilibrium distance between the two atoms, k is called the force constant and is a measure of the stiffness of the spring or bond.

The Hooke's law states *that when the atoms are displaced from their equilibrium position, the restoring force, F is proportional to the displacement and has the opposite direction.* The force constant is equal to the restoring force operating for a unit displacement from the equilibrium position.

The bonds in organic molecules have two kinds of vibrations: (i) stretching vibration and (ii) bending vibration. The ***stretching vibration*** is one in which the distance between the two bonded atoms increases or decreases, but the atoms

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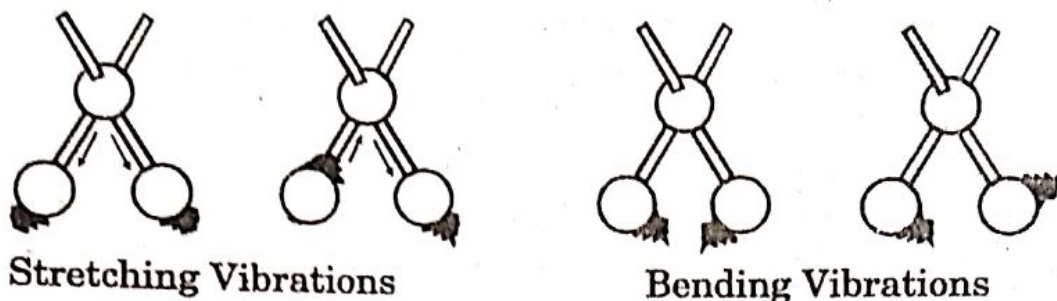
remain in the same bond axis, whereas in a ***bending vibration*** the atoms (or groups of atoms) move in such a way that causes a change in the angle between bonds with a common atom, i.e., the position of atoms changes relative to original bond axis, the interatomic distance remains unchanged.

A bending vibration of a bond requires lesser energy and thus absorbs the radiation of lower frequency than a stretching vibration of the same bond. A C – H

Stretching Vibrations **Bending Vibrations**

bending absorption occurs around 144 cm^{-1}, whereas a C – H stretching absorption occurs around 2900 cm^{-1} (in alkanes). The stretching absorptions of corresponding single (C – C), double (C = C) and triple (C ≡ C) bonds occur at 700 –1200 cm^{-1}, 1620–1680 cm^{-1}, and 2100 – 2200 cm^{-1} respectively. Thus a C ≡ C bond is stronger than C = C bond which is stronger than a C – C bond.

When infrared radiation is passed through an organic compound, some of the frequencies are absorbed and appear as absorption bands, while other do not interact with the compound and are transmitted with out being absorbed. Out of all the vibrations only those vibrations are capable of absorbing infrared radiations that cause a change in dipole moment give rise to an absorption band. The vibrations that cause a change in the dipole moment will interact with the infrared radiation and therefore, are called *infrared active vibrations.* While the vibrations that do not cause a change in the dipole moment will not interact with the infrared radiation, and therefore, called *infra inactive vibrations.*

The excitation of a molecule from the ground vibrational energy state to a higher vibrational energy state occurs only when the compound absorbs infrared radiation of a particular energy; that is a particular wavelength or frequency. In a molecule, each bond such as O – H and each group of three or more atoms such as NH_2 and CH_3 absorbs infrared radiation of certain wave numbers to give quantized excited stretching and bending vibrational states. The absorptions *depend only slightly on the molecular environmental* of the bond or group. A plot of absorbance (A) or transmittance (T) as ordinate against wavelength or wave-number as abscissa results in an *infrared spectrum* which shows a series of absorption bands (or peaks) whose positions are indicated either by wavelength (μm) or by wave number (cm^{-1}). An observed absorption band at a specific wavelength (or wave number) proves the identity of a particular bond or group of bonds in a molecule. Conversely, the absence of a certain band in the spectrum usually rules out the presence of the bond that would produce it.

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It should be noted that the stretching bands for the strongest bonds are found at the highest frequencies or shortest wavelengths, where most energy is provided. The strongest bonds are those between an H and another element, such as C, N or O. Hydrogen bonding causes a shift of the O–H stretch to lower frequencies (3600 cm^{-1} → 3300 cm^{-1}). The band also becomes broader and less intense.

The IR spectrum. An infrared spectrum can be divided into two parts.

1. Fingerprint Region. The region from 1400 to 625 cm^{-1} is called the *fingerprint region*. This region provides a set of absorption bands that is uniquely characteristic of each compound and serves as its fingerprint, therefore it is called fingerprint region. A peak-by-peak match of an unknown spectrum with the spectrum of the suspected compound in this region can be used, much like a fingerprint, to confirm its identity. An identical fingerprint region spectrum of two samples is a definite proof of their identity. Although similar but nonidentical compounds may show similar spectra in the region 4000–1400 cm^{-1} (*i.e.,* functional group region), there will be a characteristic difference in the fingerprint region. Most of the absorption bands in this region are due to bending vibrations. Stretching vibrations of C – C, C – O and C – N bonds also occur in this region.

2. Functional Group Region. The region from 1400–4000 cm^{-1} is called the functional group region. In this region most compounds have only a few strong bands, due to the characteristic stretching vibrations of their functional groups. The various functional groups absorb infrared energy at definite positions which primarily depend on whether the bonds are single, double or triple or the bond involves hydrogen as one of the bonded atoms. For example, the functional groups of X–H type (such as C–H, O – H,N – H and SH) absorb in the region 3650–2500 cm^{-1} due to their stretching vibrations. Most single bonds (e.g., C – C, C – O, C– N, C – X) absorb in the region of frequencies less than 1600 cm^{-1}; most double bonds (e.g., C = C, C = O, C = N) absorb in the region 1900–1600 cm^{-1} and most triple bonds absorb in the region 2300–2100 cm^{-1}. Thus the absorption bands in this region are very useful in determining the types of functional groups present in the molecule. Characteristic absorption frequencies (wave numbers) of some important functional groups are shown in table 1.6.

Interpretation of IR Spectra. Structural information about a compound is generally derived from the presence or absence of characteristic absorption bands of various functional groups in the IR spectrum of the compound. A knowledge of the absorption positions of the various bonds is very useful for the determination of the structure of the molecule. From the data available, it is possible to correlate the absorption frequency and the type of bond and thus to determine the functional groups present in the molecule. In order to explain the IR spectrum of a compound, start from higher frequency side. It should be noted that almost all organic compounds exhibit a peaks or groups of peaks near 3000 cm^{-1} due to C – H stretching vibrations. Fig. shows the IR spectra of some compounds. In each spectrum, the deep valleys represent wave numbers of low transmission and are therefore, absorption peaks or bands.

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Table 1.6. Characteristic IR Absorption Frequencies *i.e.*, (Peaks)

Wave number (cm^{-1})	Bond	(Remarks)
1050 – 1400	C – O	(in ethers, alcohols and esters)
1050 –1400	C – N	(in amines)
1150 – 1360	SO_2	(in sulphonic acid derivatives) 2 bands seen
1315 – 1475	C – H	(in alkanes) Bending mode
1340 – 1500	$-NO_2$	(2 bands)
1430 – 1460	$= CH_2$	(in alkanes ; Bending)
1450 – 1600	C = C	(in aromatic ring ; several peaks)
1620 – 1680	C = C	(in alkenes)
1630 – 1690	C = O	(in amides) 2 bands seen.
1690 – 1750	C = O	(in aldehydes, ketones and esters)
1700 – 1725	C = O	(in carboxylic acids)
1770 – 1820	C = O	(in acid chloride)
2100 – 2200	C ≡ C	(in alkynes)
2210 – 2260	C ≡ N	(in nitriles)
2500	S – H	
2700 – 2800	C – H	(of aldehyde group)
2500 – 3000	OH	(of COOH group)
3000 – 3100	C – H	(in part of aromatic ring)
3300	C – H	(C is acetylenic)
3020 – 3080	C – H	(C is ethylenic)
2800 – 3000	C – H	(in alkanes)
3300 – 3500	N – H	(in amines and amides)
3200 – 3600	O – H	(in H– bonded ROH)
3600 – 3650	O – H	(in alcohols and phenols)

The IR spectrum of methanol shows a broad band at about 3400 cm^{-1}, ascribable to the stretching vibration of the hydrogen-bonded alcoholic O–H group. The peak at 3000 cm^{-1} is due to C–H stretching. The peak at about 1450 cm^{-1} is due to C–H bending vibration. The peak at 1050 cm^{-1} due to the C–O stretch. It is extremely difficult and impractical to attempt an interpretation of each band in the spectrum.

The IR spectrum of 2-butanone shows a peak at about 2800 cm^{-1} due to C–H stretching vibration. The peak at 1700 cm^{-1} is due to stretching of C = O group. The peak at about 1300 cm^{-1} is due to C–H bending vibration.

The IR spectrum of isobutylamine shows a peak at about 3500 cm^{-1} is due to N–H stretching. The peak at about 2800 cm^{-1} is due to C–H stretching. The peak at about 1650 is due to $N{<}^{H}_{H}$ bending vibrations. The two peaks at 1370–1400 cm^{-1} and at 1170 cm^{-1} are due to $CH(CH_3)_2$ (*i.e.*, $>$CH isopropyl) bending vibrations. At about 500 cm^{-1}, peak is due to $N{<}^{H}_{H}$ bending vibrations.

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The IR spectrum of ethyl acetate shows a peak at about 2800 cm^{-1} due to H–C stretching. The peak at 1700 cm^{-1} is due to stretching of the >C=O (carbonyl) group. The two peaks at 1400–1500 cm^{-1} are again due to C–H bonds (bending vibrations). The peak at 1250 cm^{-1} is due to the C–O stretch.

The IR spectra of alkanes show a peak at 2850–3000 cm^{-1} (i.e., below 3000 cm^{-1}) due to the C–H stretching vibrations. The C–C stretching absorption have variable frequencies and are usually weak. Methyl ($-CH_3$) and methylene ($-CH_2-$) groups normally have characteristic C–H bending vibrations at 1400–1470 cm^{-1}.

The IR spectra of alkenes show a peak at 3000–3100 cm^{-1} due to the C–H stretching vibrations. It also shows a peak at 1620–1680 cm^{-1} due to the C=C stretching vibrations. Absorptions arising from C–H bending vibrations are at 600–1000 cm^{-1}. The IR spectra of alkynes show C–H stretching absorption peaks at 2100–2260 cm^{-1} which are weak and will be absent if the triple bond is symmetrically substituted.

The IR spectra of benzene and its derivatives show two bands near 1600 cm^{-1} and 1500 cm^{-1} due to the stretching of the carbon–carbon bonds of the aromatic ring. The sharp peaks above 3000 cm^{-1} are due to the C–H stretching vibrations. A combination of peaks characteristic of the substituent pattern of the benzene ring, due to the ring C–H bending vibrations occur in the region 700–900 cm^{-1}.

IR spectra of the carbonyl group of aldehydes and ketones show very strong C = O stretching bonds in the 1665–1780 cm^{-1} region. The –CHO group of aldehyde also show two weak bands in the 2700–2775 cm^{-1} region. The exact position of the carbonyl peak depends on the nature of the substituents on the carbonyl groups, *e.g.*, in aldehydes, carboxylic acids, esters, etc.

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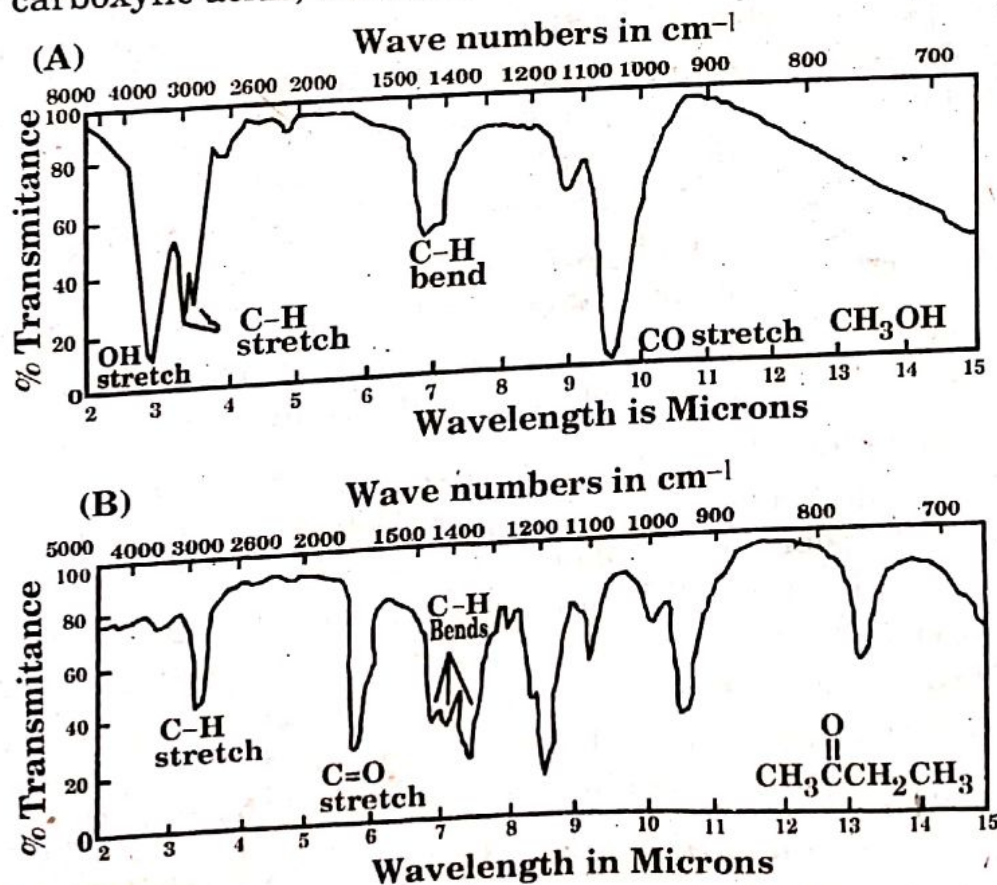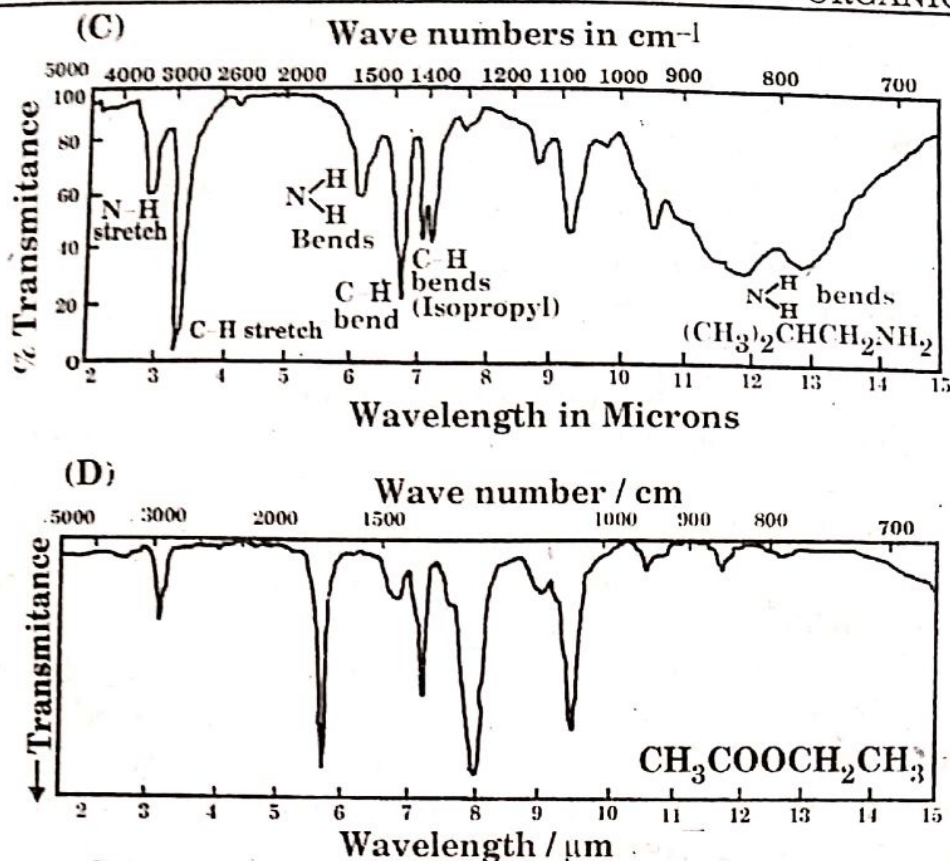
Fig. 1.17 Some IR spectra: (A) Methanol, (B) Butanone, (C) Isobutylamine, (D) Ethyl acetate

Sample Handling

Preparation of Samples: One of the most important features of *IR* spectroscopy is that a wide variety of samples can be examined by this technique. Gases, solids and liquids or solutions can all be handled and used for the measurement of their *IR* spectra. A number of methods can be employed to maintain fixed amount of material in the path of the infrared beam. Under suitable circumstances, large crystals can be used for the study of infrared dichroism and informations regarding molecular geometry and / or the manner of packing of the molecules in the lattice can be obtained. Such studies on proteins and polypeptides have been carried out. But very little has been reported on the infrared dichroism of transition metal complexes. In majority of the cases the sample is isotropically distributed.

(1) *Gaseous Samples.* No prior and special preparation is needed for the measurement of *IR* spectra of gaseous samples. Usually a 10 cm long cell is used to run gaseous samples. Some spectrophotometers are provided with cells of 10 cm, 20 cm and 30 cm length. The cell is provided with the ends ground square to which infrared transparent windows are attached to give a vacuum tight seal using some thermosetting resin. Two tubes with stop cocks and ground glass joints protrude from the cell for attaching to a gas handling system. Since the cell is heated and cooled, greatest care has to be taken to avoid cracking of the windows.

Infrared spectra of a large number of organic and inorganic compounds have been measured in the gaseous phase. But only a few thermally stable transition

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metal complexes, such as metal carbonyls, cyclopentadienyl compounds and certain acetylacetone complexes etc., have been examined in the gas phase.

(2) *Liquid or Solution Samples.* Liquids are usually handled pure. Same type of cell is used for both liquids and solutions. A variety of absorption cells for liquids and solutions are commercially available. Non-corrosive and not too viscous liquids are normally measured in sealed cells to prevent undue evaporation. The cells are usually rinsed, filled and emptied with the aid of a hypodermic syringe (without needle). The cap of the cell is plugged with an inert plastic, such as Teflon. Highly viscous liquids are often simply sandwiched as a layer between two salt plates.

It is describable to measure the infrared spectra of solutions by filling a second cell of the same thickness as the sample cell with solvent and placing the second cell in the reference beam. This will eliminate the absorption bands of the solvents.

(3) *Solids.* A wide variety of techniques is used for measurement of infrared absorption spectra of solid materials. Solid samples may be used in the form of a solution, powder, film or pellet.

(a) *Solids Run in Solution.* If the solid is soluble in some suitable solvent, its solution can be made and run in one of the cells for liquids. However, suitable solvents are limited in number and none are totally transparent. Carbon disulphide is transparent below 133 nm while carbon tetrachloride is transparent above 133 nm. Hence, at least two different solvents must be used if the complete spectrum of the solid substance is desired. Care should always be taken to place a cell filled with pure solvent in the reference beam.

(b) *Solid Films.* Amorphous solid samples may be cast into films from solution on an *IR* transmitting window or solid melted between salt plates and allowed to cool into a film. This technique is not recommended for crystalline substances.

(c) *Mull-Technique.* The most convenient and routine method is called *mulling.* The powdered sample is mixed with a little heavy paraffin oil, usually medicinal grade nujol, and mulled to form a paste, which is then transferred to rock salt plate. The oil has only a few absorption bands, specifically at about 2857 cm^{-1}, 1449 cm^{-1} and 1389 cm^{-1}. CH stretching and C–H bending absorption bands occur in these regions. In order to have the complete spectrum a second mull (perfluorokerosene, halocarbon oil, etc.) must be prepared.

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Questions

1. What is chromatography. Describe briefly the classification of chromatography.
2. Describe various operation involved in paper chromatography.
3. Describe the theory of paper chromatography.
4. Write notes on paper chromatography.
5. Describe the thin layer chromatography.
6. Write notes on column chromatography.
7. Define column chromatography and discuss the technique of column chromatography.
8. What type of molecular transitions are brought about by absorption of
   (a) Ultraviolet-visible radiation (b) Infrared radiation
9. How will you distinguish between the following pairs of compounds on the basis of IR spectroscopy?
   (a) n-Hexane and 1 - hexene
   (b) 1- butyne and 2-Hexane
   (c) 2-Hexanol and 2-Hexanone
   (d) Acetaldehyde and acetone.
10. What is the effect of (i) Conjugation and (ii) Hydrogen bonding on absorption frequency of a bond. Give examples. (P.U. 2003)
11. Briefly explain the following terms: (P.U. 2002)
    (i) Chromophores (ii)Importance of stretching vibrations in IR spectroscopy.
12. What is the principle of IR spectroscopy? Show how would you distinguish between ethane, ethylene and acetylene by IR spectroscopy. (P.U. 2001)
13. Write short notes on the following.
    (i) Finger print region (ii) Woodward Fieser's rule

SHORT QUESTIONS

1. What is Chromatography?

Ans. Chromatography is the name given to the technique for the separation of mixture of solutes brought about by the dynamic partition or distribution of dissolved or dispersed materials between two immiscible phases, one of which is moving past the other.

2. How thin layer chromatography is superior to paper chromatography?

Ans. TLC is considered to be superior to paper chromatography because of its convenience and rapidity, its greater sharpness of separation and its high sensitivity.

3. Which is the most commonly used adsorbent in TLC.

Ans. Silica gel.

4. Define adsorption chromatography.

Ans. The chromatographic separation of the components in a mixture by adsorption from a mobile liquid stream onto the surface of a powdered solid

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as stationary phase is called adsorption chromatography.

5. What is partition chromatography?

Ans. Partition chromatography is a technique in which mixtures of substances are separated by means of partition between a moving solvent and a stationary liquid which is held on a suitable solid support.

6. What is meant by charge-transfer transition?

Ans. In a particular molecule when the electron is transferred from an atom or group to another atom or group, the transition is said to be *change-transfer*.

7. What types electronic transitions take place in a molecule.

Ans. In a molecule the electrons are present in various types of orbitals *e.g.*, bonding, non-bonding and antibonding. The electrons from these various levels are excited to molecular orbitals of higher energies and thus several possible excited states from the gound state to the various excited states are obtained. These are $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$.

8. Amines absorb at higher wavelength than alcohols. Why

Ans. Non-bonding electrons on N atom in amines are loosely held as compared to electrons on O atom in alcohols due to lesser electronegativity of N atom than O atom.

9. How will you distinguish between 1,3-pentadiene and 1,4-pentadiene by UV spectroscopy.

Ans. 1,3-Pentadiene will have higher λ_{max} than 1,4-Pentadiene. This is because 1,3-Pentadiene is conjugated; whereas 1,4-pentadiene is not conjugated.

10. How will you distinguish between benzene and anthracene by UV spectroscopy?

Ans. Anthracene will have higher λ_{max} than benzene this is because anthracene is more conjugated than benzene.

11. How will you distinguish between the following pairs of compounds on the basis of IR spectroscopy?
(a) Ethyl alcohol and diethyl ether (b) Acetic acid and ethyl acetate

Ans. **(a)** Ethyl alcohol shows a strong/broad absorption at 3200–3600 cm^{-1} (due to O–H bond) while ethyl acetate does not show this adsorption.

(b) Acetic acid shows a strong/broad adsorption at 2500-3000 cm^{-1} (due to O–H bond) while ethyl acetate does not show this absorption.

Multiple Choice Questions

1. Paper chromatography can be considered to be a type of:
(a) Partition chromatography (b) Adsorption chromatography
(c) Ion-exchange chromatography (d) Gas chromatography **Ans: (a)**

2. R_f is
(a) Rate of flow of solvent (b) Rate of flow of solute
(c) Rate of distance moved by solute and solvent
(d) Rate of reaction **Ans: (c)**

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3. Thin layer chromatography
(a) Take longer time for separation (b) takes less time for separation
(c) requires expensive equipment (d) requires lot of equipment **Ans: (b)**

4. The most common adsorbent used in TLC is
(a) Calcium-silicate (b) Silica gel (c) Glass beads (d) Alumina **Ans: (b)**

5. Column chromatography is
(a) Partition chromatography (b) Gas chromatography
(c) Ion exchange chromatography (d) Adsorption chromatography **Ans: (d)**

6. The possible number of infrared absorption bands is very large for polyatomic molecules. Many of these vibrations are degenerate, that is why they:
(a) occur as overtones (b) occur at the same frequency
(c) decrease over time (d) fluctuate periodically **(Ans:(*b*))**

7. The excitation of outer electrons in atoms and molecules is associated with which of the following bonds of radiation:
(a) X-rays (b) Infrared (c) ultraviolet (d) Gamma rays **(Ans:(c))**

8. Which of the following phenomenons does not relate to optical spectroscopy:
(a) Emission (b) Absorption (c) Doping (d) Fluorescence **(Ans:(c))**

9. Light of wavelength 3×10^{-3} cm falls in which bonds?
(a) ultraviolet (b) visible (c) Infrared (d) Microwave **(Ans:(c))**

10. The difference in energy between different states of bond vibration in a molecule correspond to light in which region
(a) Microwave (b) Infrared (c) visible (d) ultraviolet **(Ans:(b))**

11. Which of the following may be deduced from the ultraviolet scopy of a molecule
(a) the presence of conjugated double bond
(b) the vibrational energy states of the molecule
(c) the rotational energy states of the molecule
(d) the structure of regular crystals

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2. BASIC CONCEPTS

2.1 ATOMIC ORBITALS

*An **atomic orbital** (A O) is a region in space around the nucleus of an atom in which the probability of finding an electron is maximum. Each orbital has a definite energy associated with it.* An atomic orbital surrounds a single nucleus. *s, p, d and f are atomic orbitals.* An orbital can contain maximum of two electrons and only if they have opposite spins (Pauli exclusion principle).

According to the modern theory, electron is believed to have wave properties as well as properties of a particle. Due to this dual nature of electron, it is impossible to determine accurately both the momentum and the position of an electron simultaneously (Heisenberg uncertainty principle). Thus we must use a statistical approach and speak of the probability of finding an electron within specified regions in space.

With the emergence of wave mechanics, the idea of an electron particle is replaced by the concept of the electron wave. In 1926 Erwin Schrodinger developed a **wave equation** which relates the energy of a system to the wave motion. For a one-electron system, the equation is written as;

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

Where m is the mass of the electron, E is its total energy, h is Planck's constant and Ψ is its wave function of the spatial coordinates, x, y and z. The wave function, ψ (Greek letter "psi") is such that ψ (x, y, z) represents the amplitude of the electron wave at various points in space. When the value of a wave function, Ψ is calculated for a particular point in space relative to the nucleus, its value may be a positive number or a negative number (or zero). The wave function Ψ is plus (+) in crests and minus (–) in troughs. At the nucleus it is zero; these places are called nodes. The signs are sometimes called **phase signs**.

The wave function, Ψ, by itself has no physical significance. The position of the electron cannot be precisely located at any instant but the probability distribution for its location can be calculated from the wave function, Ψ, by squaring it. The probability that the electron is found in a given small volume element dV at the position (x, y, z) is equal to the square of the wave function multiplied by the magnitude of the volume element.

$$\text{Probability} = \psi^2(x,y,z)\, dV$$

The greater the value of ψ^2 in a unit volume of space, the greater the probability of finding the electron in that volume.

The Schrodinger wave equation is a second order differential equation

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and therefore, has a large number of possible solutions. Each of these solutions is associated with a set of numbers, called **quantum numbers**, that describe the energies of electrons in atoms. Solutions of the Schrodinger wave equation also give information about the shapes and orientations of the atomic orbitals, which are directly related to the quantum numbers. These quantum numbers can be used to define the allowed orbitals and to describe the behaviour of an electron in an orbital.

Shape of the atomic orbitals

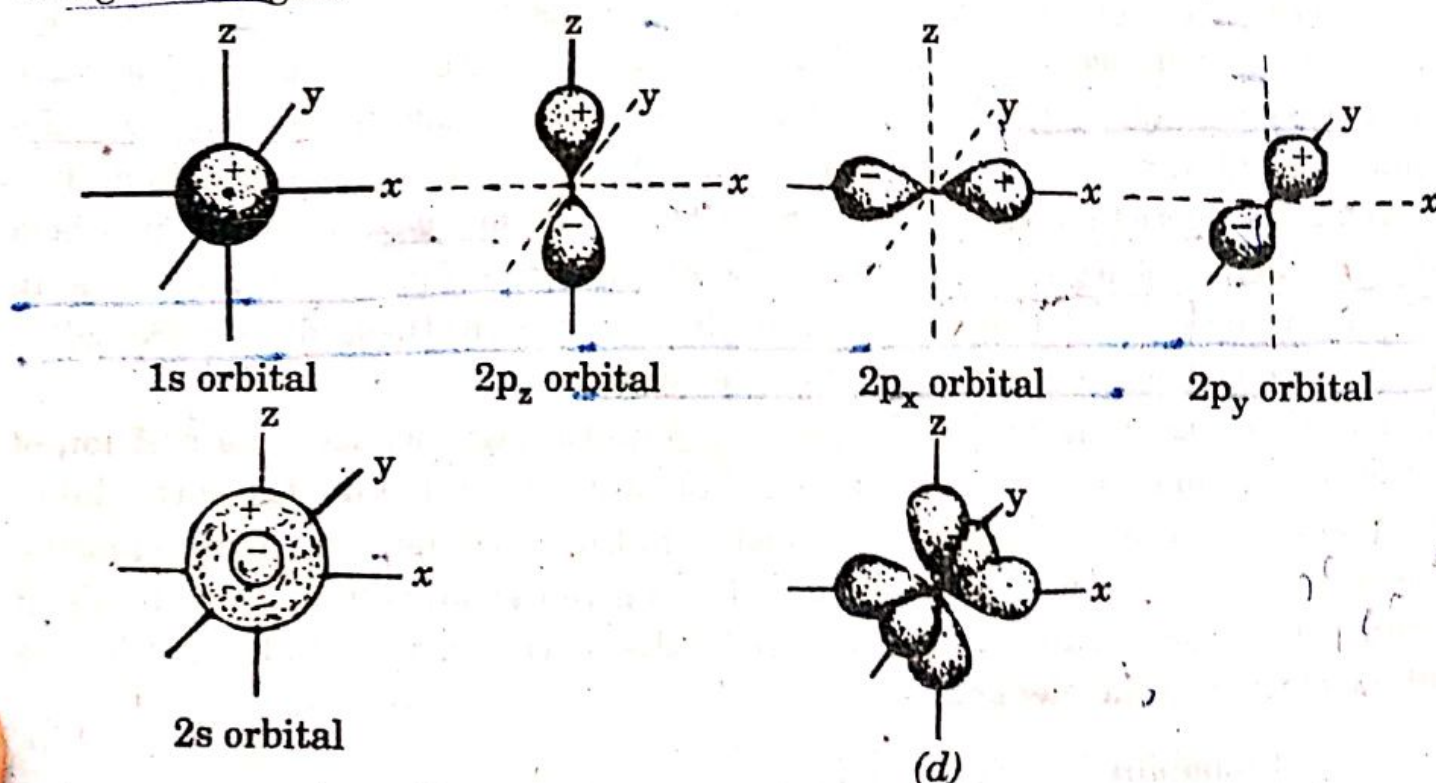
The *s* orbital is a sphere around the nucleus. In other words, *s* orbital is spherically symmetrical about the nucleus. Both 1*s* and 2*s* orbitals are spheres, but 2*s* orbital is bigger in size and has a spherical node, since 1*s* orbital is present between the nucleus and the 2*s* orbital. In the inner portion of the 2*s* orbital, ψ_{2s} is negative. A *p* orbital is dumb-bell shaped. Each *p* orbital consists of two lobes touching on opposite sides of the nucleus. There are three *p* orbitals of equal energies which are mutually perpendicular and are labeled p_x, p_y and p_z because they are oriented along the x-, y- and z-axes, respectively. In a *p* orbital there is no chance of finding an electron at the nucleus and thus the nucleus is called a **node point.** The phase sign of the wave function, ψ_{2p}, is positive in one lobe and negative in the other. The 3*s* and 3*p* orbitals are similar in shape to the 2*s* and 2*p* orbitals but of higher energies.

Assemblage of three mutually perpendicular 2p orbitals.

Fig. 2.1 Shapes of some *s* and *p* orbitals.

The 3*d*, 4*d* and 5*f* orbitals have still higher energies and quite different

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shapes and are not important for bond making in organic compounds.

Filling up of the Orbitals with Electrons

The orbitals are filled with electrons successively according to the following rules;

1. The Aufbau Principle The orbitals are filled with electrons in the order of increasing energy; the orbitals of lowest energy are filled first. The lowest energy orbital is that which has lowest value of $n + l$. If two orbitals have the same value of $n + l$, then the lowest energy orbital is that which has the lower n value. The order of increasing energy orbitals in most neutral atoms is:

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*d* etc.

2. Pauli Exclusion Principle; An orbital can have a maximum of two electrons when their spins are opposite. This principle states, *"No two electrons in an atom can have the same set of four identical quantum numbers"*.

3. Hund's Rule *When orbitals of equal energy are available, electrons occupy these singly and have parallel spins rather than in pairs.* As a result, an atom tends to have as many unpaired electrons as possible. The arrangement of electrons in various atoms is shown below:

Boron	Carbon	Oxygen
↑ — — 2p	↑ ↑ — 2p	↑↓ ↑ ↑ 2p
↑↓ 2s	↑↓ 2s	↑↓ 2s
↑↓ 1s	↑↓ 1s	↑↓ 1s
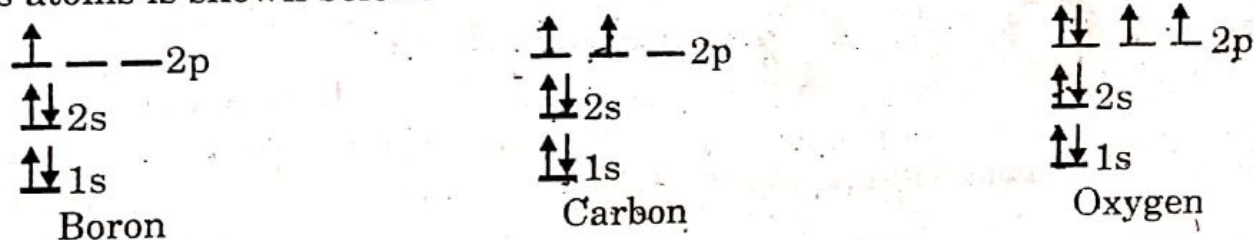
Fig. 2.2 Electronic configuration of some elements

According to Hund's rule, the number of unpaired electrons in the atom of an element is the valency of that element. Carbon has two unpaired electrons and should be divalent, but carbon is tetravalent in most of its compounds. This discrepancy had been resolved by the concept of orbital hybridization.

2.2 MOLECULAR ORBITALS (COVALENT BOND FORMATION)

A covalent bond forms by overlap of two partially filled atomic orbitals, one from each atom, is called a **molecular orbital** (MO), which embraces both atoms. The interaction of two atomic orbitals actually creats two molecular orbitals.

When atomic orbitals combine to form molecular orbitals, ***the number of molecular orbitals that result always equals the number of atomic orbitals that combine.*** Like an atomic orbital, a molecular orbital can contain a maximum of two spin paired electrons.

A covalent bond is formed between two atoms, when the two atoms come so close that a partially filled atomic orbital of one overlaps with a partially filled atomic orbital of the other. The two overlapping atomic orbitals lose their identities and lineraly combine to produce two molecular orbitals. *Orbitals which have buried in them two or more atomic nuclei are called* ***molecular orbitals.***

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A molecular orbital which is formed by the atomic orbitals of the same phase sign overlap, and has a lower energy (greater stability) than the individual atomic orbitals is called a **bonding molecular orbital,** whereas a molecular orbital which is formed by the atomic orbitals of opposite sign overlap and has a higher energy (less stability) than the individual atomic orbitals is called an **antibonding molecular orbital.** A bonding orbital which is symmetrical about a line joining the two atomic nuclei is called a **sigma** (σ) orbital and the bond is called σ bond. The corresponding antibonding molecular orbital is called a sigma star (σ*) orbital. The imaginary line joining the nuclei of the bonding atoms is the **bond axis, whose length is the bond length.** These molecular orbitals are filled with available electrons according to the same principles which are *applied* for filling atomic orbitals.
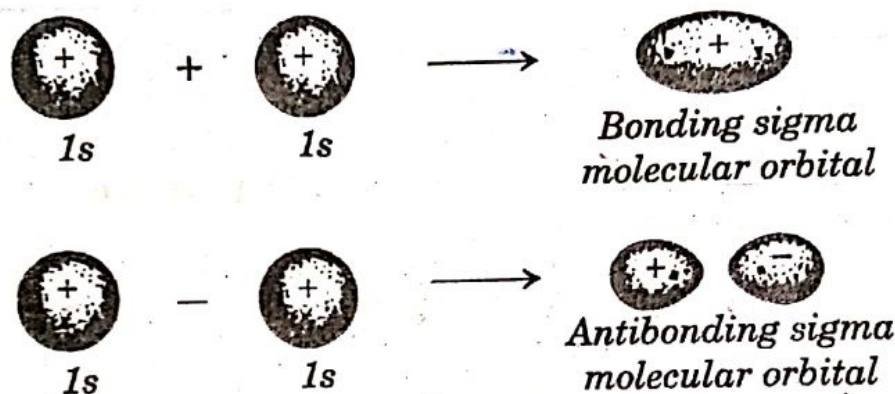
Fig. 2.3 Formation of bonding (σ) and antibonding (σ*) molecular orbitals.

"*A molecular orbital which is symmetrical about a line joining the two nuclei and is occupied by a pair of electrons is called a sigma (σ) molecular orbital and the linkage thus established is called* ***sigma bond.***

Consider the **formation of hydrogen molecule** from two hydrogen atoms. When two hydrogen atoms come close enough so that their 1*s* orbitals overlap, the two overlapping atomic orbitals linearly combine to form two molecular orbitals; a σ orbital and a σ* orbital (fig. 2.4) (Two plus signs means that the two orbitals are in the same phase and can overlap, while plus and minus signs show that the two orbitals are out of phase and therefore cannot overlap).

The two 1*s* electrons from the hydrogen atoms fill the low energy σ
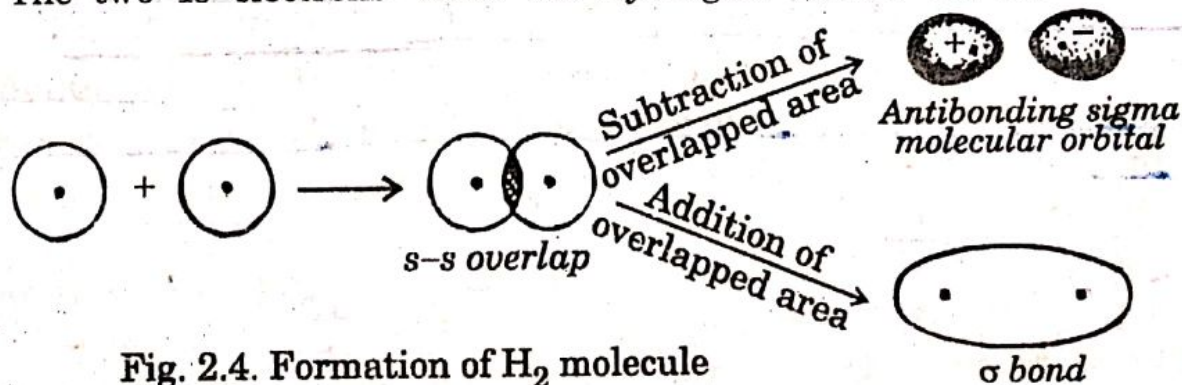
Fig. 2.4. Formation of H_2 molecule

orbital and have paired spins (↓↑). The high energy σ* remains empty. In the σ orbital the probability of finding the electron pair is maximum in the region between

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the two nuclei. Each of the two electrons accupying the σ orbital is attracted by both the atomic nuclei. Before the formation of H_2 molecule, each electron was attracted by only one nucleus.

The attractive force of the two nuclei for the two electrons in the σ orbital is more than offsets the repulsive force acting between the two nuclei and between the two electrons. This extra attractive force lowers the energy of the system (H_2 molecule). Thus 436 kJ/mol of energy is released when two hydrogen atoms combine to form a hydrogen molecule. This 436 kJ/mol is called the bond energy of H–H bond.

$$H + H \longrightarrow H-H \qquad \Delta H = -436 \text{ kJ mol}^{-1}$$

The two atomic nuclei are therefore held together by the electron pair of the σ orbital. The two electrons in the σ orbital are called σ electrons and the resulting bond is called σ bond.

In an antibonding molecular orbital, i.e., σ* orbital, the probability of finding the electrons is *minimum* in the region between the two nuclei. Thus if electrons were to occupy the antibonding orbital, the electron would avoid the region between the nuclei. Since the repulsive forces (between the two nuclei and between the two electrons) would be greater than the attractive forces of the two nuclei for the two electrons and thus the molecule would be unstable.
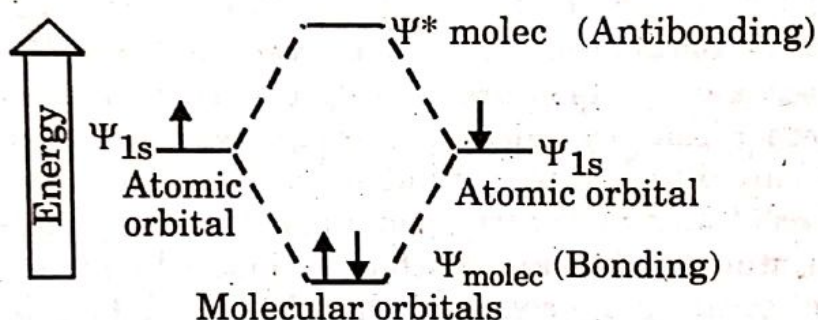
Fig. 2.5 Energy diagram for the formation of H_2 molecule

When two atoms approach each other, the nuclei of two approaching orbitals must be at an optimum or equilibrium distance to form the lowest energy (stable) molecule. In the H_2 molecule, the two nuclei are 0.074 nm apart. This distance is called the ***bond length.***

From the above discussion it is obvious why a two electron covalent bond is specially stable. If there are three or four electrons available, the extra electrons will occupy the antibonding σ* orbital which will make the system unstable. Similarly, a one electron σ bond (i.e, a single electron in the σ orbital) will not be as strong as a two electron σ bond because the electron bond will be relatively weaker in the former case.

A σ bond is also formed between two atoms when a *p* orbital of one atom overlaps with *s* orbital of the other (*s* – *p* overlap) or when a *p* orbital of one atom overlaps with a *p* orbital of the other (*p* – *p* overlap), provided the axes of the two overlapping atomic orbitals form a straight line and have the same phase signs.

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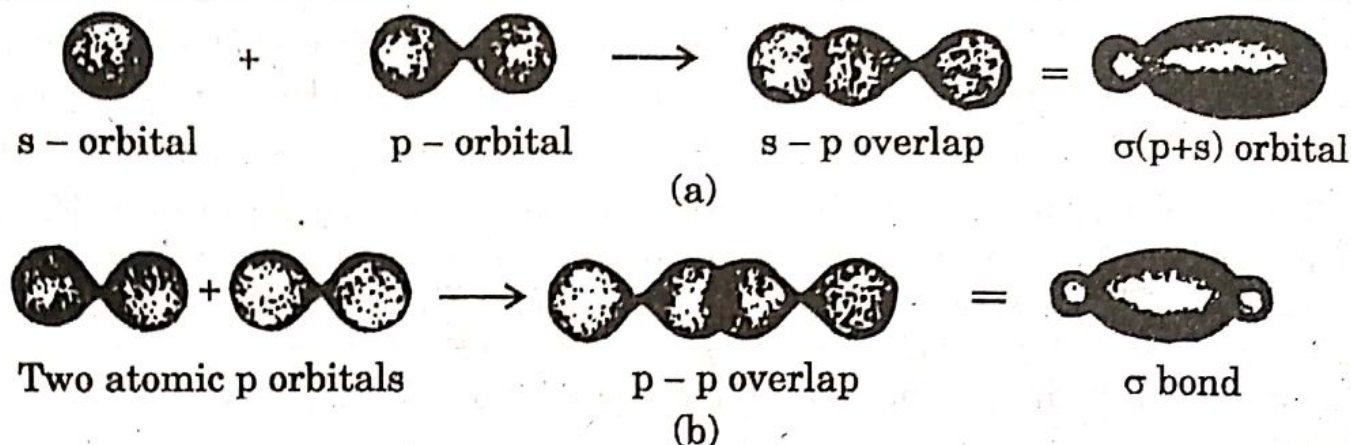
Fig. 2.6. (a) s – p overlap (b) p – p overlap

Molecular orbitals may be formed by the overlap of any kind of atomic orbitals (*s*, *p* or *d*) whether they are same or different, but the two lobes that overlap must have the same sign. However the extent of overlap depends upon the atomic orbitals involved.

Pi (π) Bond

Besides the σ bond, a π bond can also exist between two atoms. A π bond is formed by parallel or side-to-side overlap of *p* orbitals. When two *p* orbitals on two different atoms which are already bonded by a σ bond, have their axes parallel to each other and are coplanar, overlap, two new molecular orbitals are formed whose shapes are different from σ and σ* orbitals. The bonding molecular orbital is called a pi (π) orbital and the corresponding antibonding molecular orbital is called a pi star (π*) orbital. The bonding π orbital results when *p* orbital lobes of same sign overlap; the antibonding π* orbital results when p orbital lobes of opposite sign overlap. The π orbital has two regions of electrons density above and below the plane containing the two nuclei and this plane is a nodal plane (plane of no electron density) for π orbitals. The two electrons from the two overlapping *p* orbitals fill the low energy π orbital and are called π electrons. The resultant bond is called a π bond. The π bond is not as strong as the σ bond, because of a relatively small overlap in the former case. This is why, whenever possible, the orbitals will overlap in the σ manner to allow for maximum overlap of atomic orbital. The antibonding π* orbital is of higher energy and it is not occupied by electrons when the molecule is in the ground state. A π* orbital has two nodal planes, one passing between two atoms and the other perpendicular to it.

"A molecular orbital formed by the side-wise overlap of two half-filled orbitals and having one and only one nodal plane containing the nuclear axis is called π molecular orbital (π MO)".
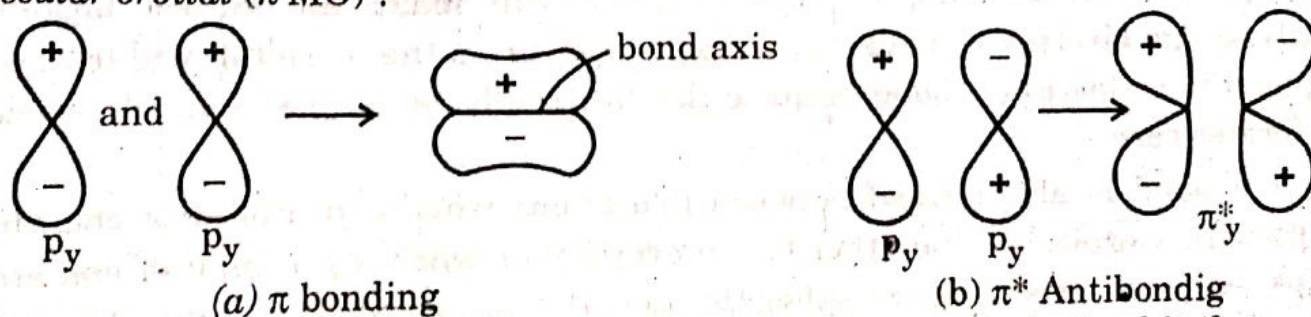
Fig. 2.7. The interaction of *p* orbitals to form π and π* orbitals

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Difference between sigma and pi bonds

Sigma bond	Pi bond
1. It is formed by head - to head overlap of atomic orbitals.	1. It is formed by lateral(sidewise) overlap of p orbitals (or p or d orbitals).
2. It has a single region of electron density between the two nuclei.	2. It has two regions of electron density above and below the nuclei.
3. Rotation of atoms about a σ bond occurs freely.	3. Rotation of atoms is not possible around a π bond.
4. It has lower energy.	4. It has higher energy.
5. Only one bond can exist between two atoms.	5. One or two bonds can exist between two atoms.
6. The overlap is more effective.	6. The overlap is not as effective as in σ bond overlp.

2.3 Hybridization of Atomic Orbitals. 2014 1(V)

The process of mixing of atomic orbitals of different types (s,p, d, etc) of the same atom to give a set of new equivalent orbitals is called **hybridization.** These new orbitals are called **hybrid orbitals** and the number of hybrid orbitals is equal to the number of atomic orbitals combined. The hybrid orbitals arise only during the process of bonding and do not exist in the free atom. Orbital hybridization occurs in the excited state.

Many elements, for example, Be, B and C, form compounds whose formation cannot be explained on the basis of the configuration of the elements in the ground state. However, a satisfactory description of compounds of these elements can be obtained through an orbital hybridization approach. The atomic orbitals of carbon can be hybridized in three different ways depending upon the number of atoms bonded to the carbon atom.

The electronic configuration of carbon in its ground or atomic state is $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$. It has only two unpaired electrons (partially filled orbitals) which can form only two covalent bonds, but carbon forms four bonds in the majority of its compounds. Its tetravalency can be explained by assuming that an electron from the 2*s* orbital is promoted to an empty $2p_z$ orbital giving the excited state a configuration $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$. In its excited state, carbon can form four bonds but these would not be equivalent. Three *p*-orbitals would form the bonds along the three mutually perpendicular axes, whereas the fourth bond arising from 2*s* orbital would be non-directional because *s* orbitals are spherically symmetrical. This shows that two different types of C–H bonds are involved in the formation of CH_4 molecule. In actual practice, all the four bonds in CH_4 are equivalent with a bond angle of 109.5°. This has been explained by the process of hybridization in which 2*s*

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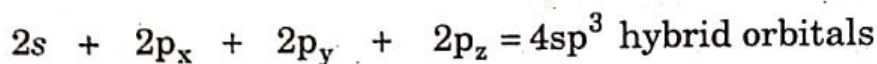
and three $2p$ orbitals (p_x, p_y and p_z) in the excited state are mixed to form a set of four equivalent hybrid orbitals.

$$2s + 2p_x + 2p_y + 2p_z = 4sp^3 \text{ hybrid orbitals}$$

*The process of combining the s and the three p orbitals to get four sp^3 orbitals is called **sp^3 hybridization.*** The symbol sp^3 signifies that each sp^3 orbital is made up of s and p orbitals in the ratio of 1:3. The sp^3 orbitals are directed from the center of a regular tetrahedron to its four corners, making an angle of 109.5° with each other. The sp^3 hybridization is therefore, also called **tetrahedral hybridization.** These sp^3 orbitals are non-coplanar (do not lie in the same plane). The small lobe is often omitted when depicting hybrid orbitals.

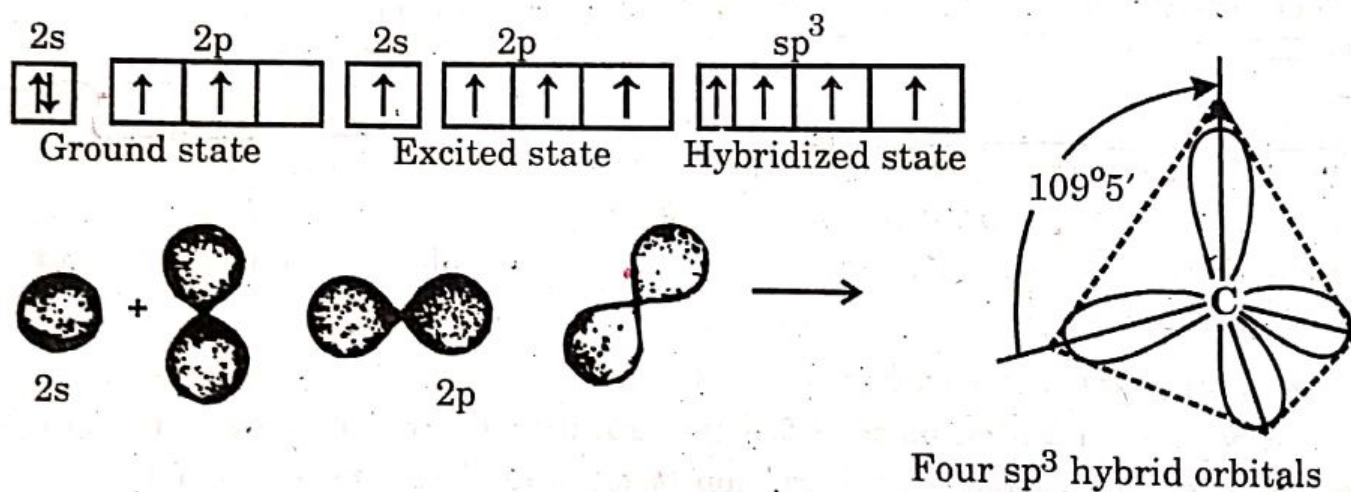



Fig. 2.8 Hybridization of s and three p orbitals to form $4sp^3$ hybrid orbitals.

The methane molecule is formed by the overlap of four sp^3 orbitals of carbon with 1s orbitals of four hydrogen atoms. The methane molecule contains four σ bonds, each due to sp^3–s overlap and each H–C–H bond angle = 109.5° (tetrahedral). The sp^3 hybridization occurs when carbon is bonded to four other atoms.

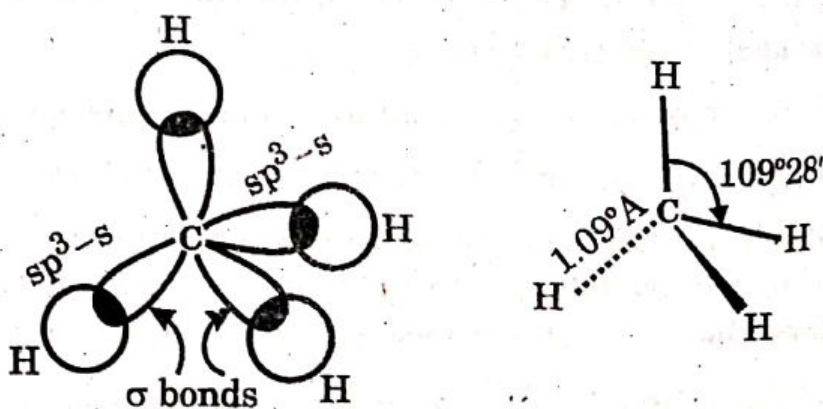



Fig. 2.9 Bonding in methane

The promotion of an electron from the 2s to a 2p orbital requires energy 406 kJ mol^{-1}, but by doing this carbon forms four covalent bonds *instead of two bonds* and releases energy 887 kJ mol^{-1}. The formation of two additional bonds releases energy more than compensate for that required to excited the electron.

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2.4 Multiple (localized) Bond: Trigonal and digonal Hybridization

Trigonal or sp^2 Hybridization. When carbon is bonded to only three other atoms as in ethene, C_2H_4 (one carbon and two H atoms), the 2*s* and two of the three 2*p* orbitals of each carbon atom are hybridized to give three equivalent sp^2 hybrid orbitals of each carbon, leaving the remaining 2*p* orbital unhybridized. Each sp^2 orbital is composed of *s* and *p* orbitals in a ratio of 1:2. These three sp^2 orbitals lie in the same plane and make an angle 120° with each other, the unhybridized 2*p* orbital is perpendicular to this plane. The sp^2 hybridization is, therefore, also called trigonal hybridization.

Fig. 2.10 (a) The $3sp^2$ orbitals (b) Bonding in ethene

In ethene, two sp^2 hybridized carbon atoms form a σ bond between them by the overlap of one sp^2 orbital from each carbon, the remaining two sp^2 orbitals of each carbon form σ bonds to four hydrogen through overlap with the 1*s* orbitals of the hydrogen atoms.

The two unhybridized *p* orbitals one on each carbon are perpendicular to the axis joining the two carbon nuclei and their axes are parallel. These two *p* orbitals are in a perfect position to overlap laterally (side-to-side), to generate two new molecular orbitals, i.e., a bonding π orbital and an antibonding π* orbital. The electrons fill the low energy bonding π orbital leaving the high energy antibonding π* orbital empty. This sidewise overlap of *p* orbitals results a pi (π) bond. Thus carbon – carbon double bond consists of two different kinds of bonds, a σ bond and a π bond. The π bond is more diffused and is weaker than that of σ bond.

Fig. 2.11. Formation of π bond in ethene

sp hybridization

When each carbon atom (as in acetylene) is bonded to only two other atoms, the 2*s* orbital and one 2*p* orbital of carbon are hybridized to form 2*sp* hybrid orbitals, leaving two 2*p* orbitals as unhybridized. The axes of the two *sp* orbitals form a straight line. The angle between the two *sp* orbitals is thus 180°. The *sp* hybridization is, therefore, called ***linear or diagonal hybridization***. The two

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unhybridized $2p$ orbitals are perpendicular to the axis that passes through the centre of the $2sp$ orbitals.

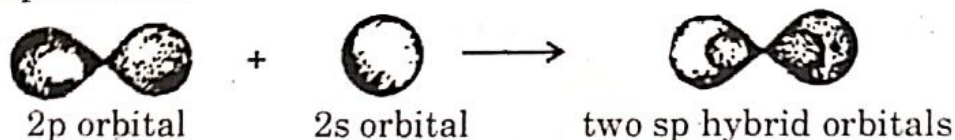



Fig. 2.12 Formation of *sp* hybrid orbitals.

In acetylene, H–C ≡ C–H two *sp* hybrid orbitals (i.e., one from each carbon) overlaps to form a σ bond between them. The remaining two *sp* orbitals at each carbon overlap with 1*s* orbitals from hydrogen atoms to produce two sigma (σ) C–H bonds. The residual two 2*p* orbitals on each carbon also overlap side-to-side to form two π bonds. Thus in acetylene there is one σ bond and two π bonds between the two carbon atoms.

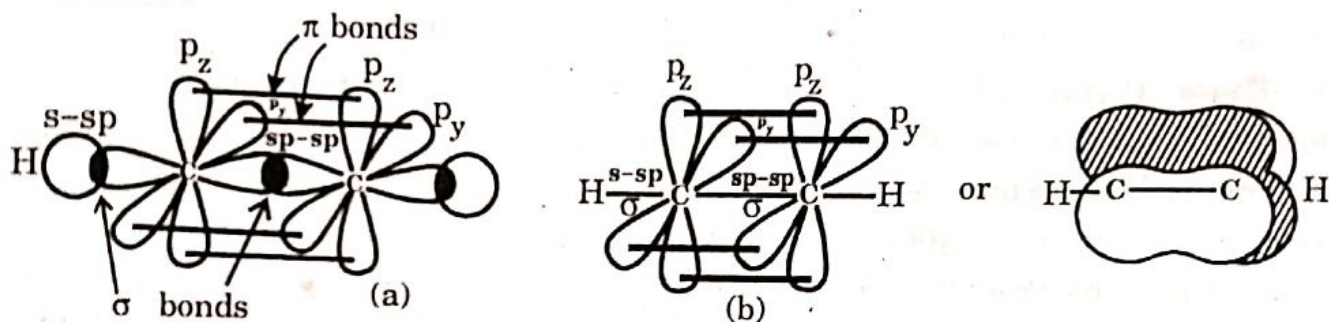
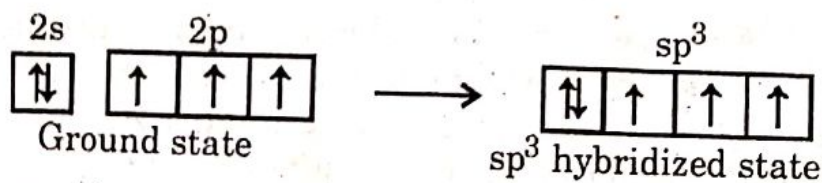



Fig. 2.13. (a) bonding in acetylene (b) Formation of two π bonds in acetylene

The formation of a double bond between carbon and oxygen and a triple bond between carbon and nitrogen can be explained in a similar manner.

Hybridizations of Nitrogen

Nitrogen has five electrons in its valence shell; $2s^2, 2p_x^1, 2p_y^1, 2p_z^1$. Like carbon, the nitrogen atom also undergoes sp^3, sp^2 and sp hybridization. Whenever nitrogen is attached to three other atoms or groups (as in ammonia and methylamine), then 2*s* and three 2*p* *orbitals* (p_x, p_y and p_z) mixed to form four equivalent hybrid orbitals.

The four sp^3 orbitals of nitrogen are directed towards the corners of a regular tetrahedron, just as the sp^3 orbitals of carbon do. Consider the formation of methylamine. In methylamine both nitrogen and carbon are sp³ hybridized. One of the sp³ orbitals of nitrogen is completely filled and cannot take part in bond formation. The C – N σ bond in CH_3NH_2 is formed by overlap of an sp^3 orbital of

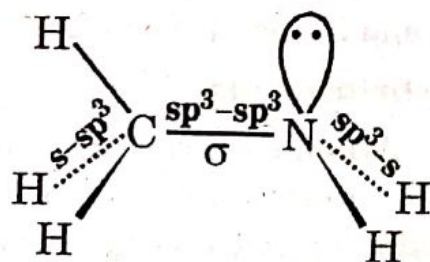



Fig. 2.14 Structure of methylamine

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nitrogen and sp^3 orbital of carbon . Each N – H σ bond is formed by the overlap of an sp^3 orbital of N and s orbital of hydrogen. Each C – H σ bond is formed by overlap of an sp^3 orbital of carbon and s orbital of hydrogen. All bond angles are approximately tetrahedral. The H – N – H bond angle in methylamine is however, 105.9° which is slightly less than the normal tetrahedral angle of 109° 28′. This is because the sp^3 orbital containing the unshared pair of electrons is somewhat larger than those containing bond pairs. Thus the angles between the σ bonds on the other side of molecule are compressed slightly. In CH_3NH_2 the N–H bond length is 1.011A° and the C–N bond length is about 1.47A° in different amines.

Also, nitrogen can form compounds using sp^2 and sp hybrid orbitals. Whenever nitrogen is bonded to two other atoms or groups (as in imines or azo compounds), it uses two sp^2 hybrid orbitals plus the unhybridized p_z orbital to form its bonds.
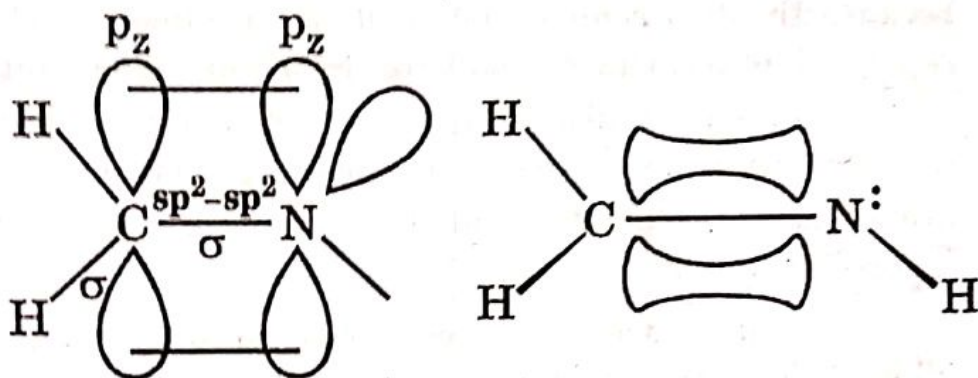
Fig.2.15.Bonding in CH_2 = NH. Both C and N are sp² hybridized

Whenever nitrogen is bonded to only one other atom or group of atoms (as in H–CN, methyl cyanide, or nitrogen), it uses an sp hybrid orbital plus the two unhybridized 2p orbitals (p_y and p_z) to form its bonds as shown in Fig. 2.17.
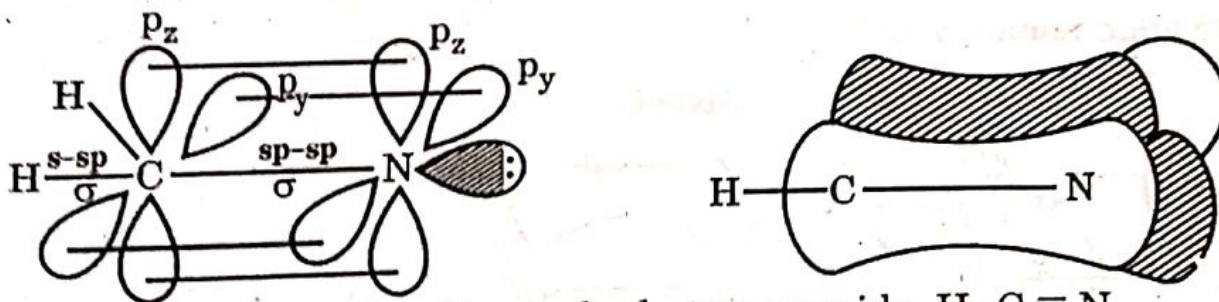
Fig. 2.16 Bonding in hydrogen cyanide, H–C ≡ N

Hybridizations of Oxygen

Oxygen has six electrons in its valence shell; $2s^2, 2p_x^2, 2p_y^1, 2p_z^1$. Like carbon or nitrogen, the oxygen undergoes sp^3 and sp^2 hybridizations. Whenever oxygen is bonded to two other atoms or groups (as in water, ethers, or alcohols or phenols), then 2s and three 2p orbitals $(p_x, p_y$ *and* $p_z)$ mix to form 4sp³ equivalent hybrid orbitals.

2s	2p$_x$	2p$_y$	2p$_z$		4sp³			
⇅	⇅	↑	↑	⟶	⇅	⇅	↑	↑
Ground state					sp³ hybridized state			

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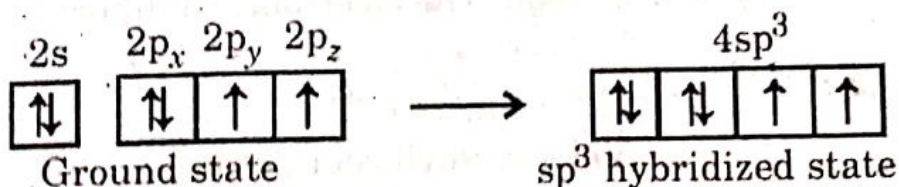
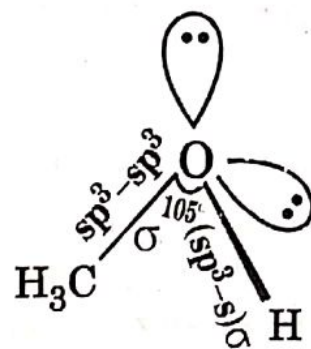

The four sp^3 hybrid orbitals of oxygen are directed towards the corners of a regular tetrahedron, just as the sp^3 orbitals of carbon or nitrogen.

In methanol both carbon and oxygen are sp^3 hybridized. Two of the sp^3 orbitals, are completely filled and cannot take part in bond formation.

The C–O bond in methanol is formed by overlap of an sp^3 orbital of carbon and an sp^3 orbital of oxygen. The O–H bond is formed by overlap of an sp^3 orbital of oxygen and *s* orbital of hydrogen. The C–O–H bond angle is 105°, which is less than the normal tetrahedron angle. This is because the two completely filled sp^3 orbitals of oxygen repel each other, which results in reduction of bond angle.

Structure of methanol

Oxygen can also form compounds using sp^2 hybrid orbitals. Whenever oxygen is bonded to one other atom or group (as in aldehydes and ketones) it uses sp^2 orbitals plus the unhybridized p_x orbital to form its bonds.

In aldehydes and ketones, the carbonyl group, like the C–C double bond of alkenes, is composed of one σ bond and one π bond. Both the carbon and oxygen are sp^2 hybridized. The σ bond is formed by the overlap of an sp^2 orbital of carbon and an sp^2 orbital of oxygen. The π bond is formed by the overlap of unhybridized *p* orbitals of the two atoms. The two unshared electrons pairs of oxygen occupy the sp^2 hybrid orbitals of oxygen. Becauses the carbonyl carbon is sp^2 hybridized, the three atoms attached to it lie in the same plane. The bond angles between the attached atoms are approximately 120°.

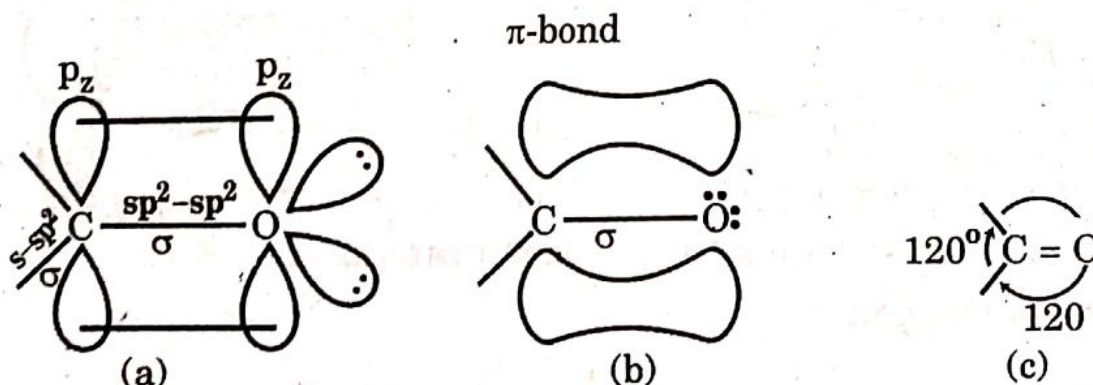
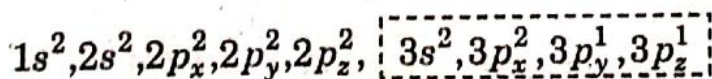



Fig. 2.17 Bonding in aldehydes and Ketones

Oxygen does not undergo *sp* hybridization.

Hybridization of Sulphur

Atomic number of sulphur is sixteen. The electronic configuration of sulphur is

$$1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2, \boxed{3s^2, 3p_x^2, 3p_y^1, 3p_z^1}$$

Valence shell configuration

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The sulphur undergoes sp^3, sp^2 and sp^3d^2 hybridizations. In sp^3 hybridization, $3s$, $3p_x$, $3p_y$, $3p_z$ atomic orbitals of the valence shell of sulphur combine to form four sp^3 hybridized orbitals. Two of these hybridized orbitals contain two electrons each (the lone-pair electrons), while the other two are singly occupied. In the formation of thiol molecule RSH, one singly occupied sp^3 orbital of S-atom overlaps with the sp^3 orbital of R group to form a σ (sigma) bond. The second singly occupied sp^3 orbital of S overlaps with $1s$ orbital of H atom to form another σ bond.

Since in thiols sulphur is sp^3 hybridized, the <R–S–H should be normally 109.5°. But the actual <RSH is shrink to a much less value; 99.4° in case of CH_3SH. This is attributed to the fact that the lone pair-lone pair interactions overshadow to some extent the bond pair-bond pair repulsions of S–R and S–H bonds. As a result <RSH is reduced considerably.
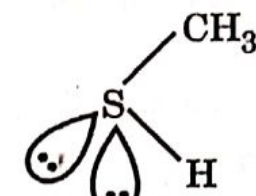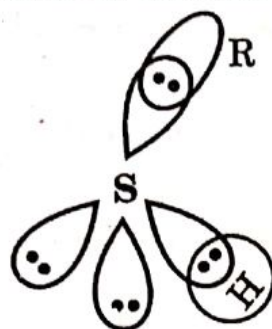
Fig. 2.18 Bonding in thiol

In dimethyl sulphide, $(CH_3)_2S$, sulphur is also sp^3 hybridized, two sp^3 orbitals are occupied by bonding pair of electrons and two by lone pairs.

pπ–dπ bonding (π_{d-p} bond)

In general, atoms of the second row of the periodic table do not form stable bonds of the type discussed in ethene and acetylene (π bonds formed by overlap of parallel p orbitals). However, there is another type of double bond that is particularly common for the second row atoms, sulpur and phosphorus. For example, such a double bond is found in dimethyl sulfoxide, $(CH_3)_2S=O$, and dimethyl sulphone, $(CH_3)_2S(=O)_2$, in which sulphur is sp^3 hybridized. In $(CH_3)_2S=O$, the two methyl groups (R groups) are bonded to sulphur by σ bonds using two sp^3 orbitals; the O atom is bonded to S by a σ bonds using third sp^3 orbital and a π_{d-p} bond (one of the sulphur electron is promoted to 3d orbital); a lone pair occupies the fourth sp^3 orbital of sulphur. In sulphones, there are four σ bonds to four sp^3 orbitals of sulphur and two π_{d-p} bonds, one to each oxygen atom.

When sulphur is bonded to six other atoms as in SF_6, then S atom uses all the six valence shell electrons in forming six S–F σ bonds.

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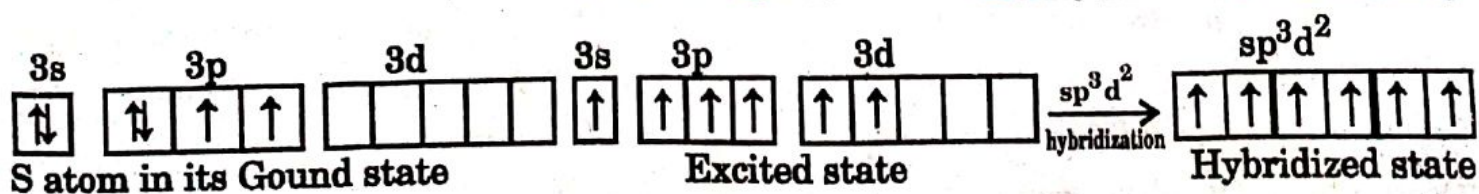
One s (3s), three p ($3p_x$, $3p_y$ and $3p_z$) and two d (3d) orbitals of sulphur undergo sp^3d^2 hybridization to form six equal energy hybrid orbitals which are directed toward the corners of regular octahedron. Each hybrid orbital contain one electron. Each sp^3d^2 hybrid orbital is overlapped by a half-filled 2p orbital from fluorine to form a total of six covalent bonds.
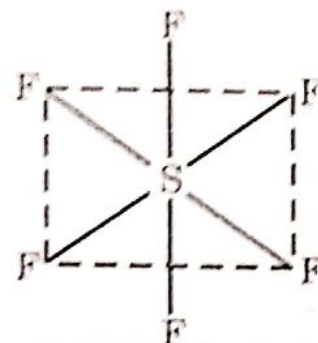
Fig. 2.19 Octahedral shape of SF_6 molecule

Examination of the octahedral molecule shows that F–S–F bond angles are 90° and 180° and the bonds are quite polar. Because the molecule is symmetrical, the large bond dipoles cancel, and the molecule is nonpolar.

We have described the localized chemical bonds that are constituted from overlap of two atomic orbitals and are centered around two nuclei. *Bonds in which the bonding electrons are shared by only two nuclei in a molecule* are called **localized bonds.** A single covalent bond is called sigma (σ) bond. In multiple localized bonds both the σ and π electrons are confined between only two atoms (i.e; nuclei). In other words the electron density is concentrated between only two atoms. Compounds which have localized bonds can be described by a single Lewis structure. Also the predicted bond lengths, bond energies and dipole moments agree fairly with the experimentally observed values. Their chemical reactivity and spectral behaviour is also predictable.

Difference between an AO, a hybrid AO, a MO and a localized MO.

An atomic orbital is a region of space in an atom in which an electron may exist. A hybrid atomic orbital is mathematically fabricated (made up) from some number of atomic orbitals to explain equivalency of bonds. A molecular orbital is a region of space about the *entire molecule* capable of accommodating electrons. A localized molecular orbital is a region of space between a pair of bonded atoms in which the bonding electrons are assumed to be present.

2.5 Properties of Chemical Bonds

(i) Bond Angles

Bond angle *is the mean angle formed by the two imaginary lines that connect the central atom with the two atoms on either side of it.* For example, in the water molecule H–O–H, the bond angle is the angle formed by the lines representing the two O–H bonds, and H–O–H bond angle is 104.5°.

Bond angles at carbon are predicted by hybridization and the bond angles of sp^3 carbon would always be the tetrahedral angle 109.5°, when four attached atoms at carbon are identical as in CH_4 or CCl_4. In most cases the angles deviate a little from the pure tetrahedral value. For example, the C–C–Br in 2-bromopropane is

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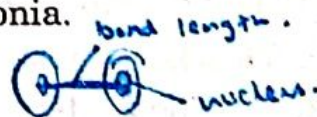
114.2° and $C-CH_2-C$ is 112°. Similarly, slight variations are generally found from the ideal values of 120° and 180° for sp^2 and sp carbon respectively. These deviations occur because of slightly different hybridization, i.e., a carbon bonded to four other atoms hybridizes one s and three p orbitals, but the $4sp^3$ hybrid orbitals thus formed are generally non-equivalent, each sp^3 orbital does not contain exactly 25% s and 75% p character. Because the four atoms have different electronegativities, each makes its own demand for electrons from the carbon atom. The carbon atom gives more p character when it is bonded to a more electronegative atoms. For example, in CH_3Cl, the C–Cl bond has 77.5% p character and C–H bond has 72.5% p chracter. The inter-orbital angle decreases with the increasing p chracters of the orbitals. Therefore, in CH_3Cl, $H-C-Cl$ angle is 108° whereas H–C–H angle is 111°. We have seen above, it is possible for the hybridization or orbital mixing, at carbon to occur in asymmetric fashion (more s mixed with p in some orbitals than in others) in order best to accommodate different substituents.

Atoms with unshared pairs of electrons follow the same hybridization pattern as asymmetrically substituted carbon. For example, an sp^3 hybridization scheme produces good agreement for the bond angles in H_2O and NH_3. In these compounds, oxygen and nitrogen hybridize their 2s and 2p to form four sp^3 hybrid orbitals and then use only two (or three) of these for bonding with hydrogen, the others remaining occupied by unshared pairs. As we have seen above, an atom supplies more p character when it is bonded to more electronegative atoms. An unshared electron pair may be considered to be an "atom" of the lowest possible electronegativity. Consequently, the orbitals with the unshared pairs of electrons have more s character and the O–H (or H–N–H) bond orbitals have more p chracter than pure sp^3 orbitals and the angles H–O–H (or H–N–H) are slightly smaller than tetrahedral angle 109.5°. The observed H–O–H bond angle in water is 104.5° and H–N–H bond angel in ammonia is 107.2°. The oxygen with two lone pairs in water supplies more p character than the nitrogen with one lone pair in NH_3, therefore, the bond angle in water is still smaller than in ammonia.

bond length.
nucleus.

(ii) Bond Lengths

*The mean distance between the centres of the nuclei of two bonded atoms is called **bond length.*** The distance between the atoms of a bond does not remain constant since the atoms are always vibrating with respect to each other in a molecule; the measured bond distance is therefore an average value. Bond lengths are measured by X-ray crystallography and by microwave spectroscopy. In SI units it is expressed in nanometer, nm (1nm = 10^{-9} m), previously the unit angstrom (1A° = 10^{-10} m) was used.

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The bond length between two given atoms remains constant fairly in different molecules, the variation is less than 1%. In most of the compounds, the C–C single bond length is about 0.154 nm and C–H bond length is 0.108 nm. The C–C bond distance in $H_3C-CH_3, CH_3-CH_2-CH_3, CH_3-CH_2Cl$ are 0.154 nm, 0.154 nm and 0.155 nm respectively. Similarly, the C – Cl bond length is 0.175 nm in CCl_4 and 0.177 nm in CH_3-Cl. Deviations from the normal bond lengths give important information about the structure of compounds.

"One half of the bond length between two similar atoms is called the covalent radius of that atom." For example, the covalent radius of carbon is 0.077nm which is one half of the C – C bond length (0.154 nm). Similarly the covalent radii of chlorine (0.099 nm) and hydrogen (0.037 nm) are one-half respectively of the Cl–Cl (0.199nm) and H–H (0.074 nm) bond lengths. *The covalent radii can be used to calculate the bond lengths between the unlike atoms which,* in some cases, the bond lengths between unlike atoms are not equal to the sum of the covalent radii of the two bonded atoms. For example, the C–Cl bond length in H_3C-Cl is 0.176 nm which is equal to the sum of the bond radii of carbon (0.077 nm) and chlorine (0.099 nm). Similarly the C – H bond distance in ethane is 0.109 nm. However in most cases, the bond lengths between unlike atoms are not equal to the sum of the covalent radii of the two bonded atoms. For example, the observed C – N bond length (in CH_3NH_2) is 0.147nm, whereas the sum of the covalent radii of carbon and nitrogen is 0.151nm. Similarly, the observed C – O bond length in ethanol is 0.141nm, although the sum of the covalent radii carbon and oxygen is 0.150nm. *In general, the shrinkage in bond length becomes more and more marked as the difference between the electronegativities of the two bonded atoms increase.*

Bond length is also affected by nature of hybridization of the bonded atoms. A large fraction of *s* character means a shorter bond. The hybridization effect can be seen in a series of C – H bonds. The C–H bond lengths in C_2H_6 (C atom is sp^3), C_2H_4 (the C is sp^2) and C_2H_2 (the C is sp) are 0.110 nm, 0.107nm and 0.106nm respectively. This is because the hybrid orbital with increased *s* character is held more strongly by the nucleus.

A single bond is longer than a double bond, and a double bond is longer than a triple bond between the same two atoms. For example, the C – C bond length in C_2H_6 is 0.154nm, while the C = C bond length in C_2H_4 is 0.134 nm and the C≡C bond length in C_2H_2 is 0.120 nm. The shrinkage of the multiple bonds is due to the presence of extra π electrons between the two nuclei which exert additional attraction on the nuclei and thus nuclei come closer to each other.

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Table 2.1 Bond lengths and Bond Energies

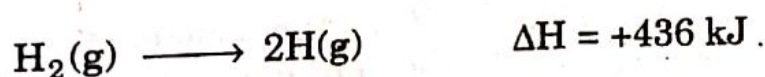
Bond	Bond length (nm)	Bond energy kJ/mole	Bond	Bond length (nm)	Bond energy kJ/mole
H – H	0.074	436	C – O	0.143	358
C – H	0.108	414	C = O	0.122	740
C – C	0.154	345	C – N	0.147	305
C = C	0.134	610	C = N	0.128	615
C ≡ C	0.120	835	C ≡ N	0.116	891
C – F	0.138	450	N – H	0.101	391
C – Cl	0.177	326	N – N	0.145	163
C – Br	0.194	276	N ≡ N	0.110	945
C – I	0.214	240	O – H	0.096	464
O – O	0.148	146	H – Cl	0.127	431
O = O	0.121	498	H – Br	0.141	365

(iii) Bond Energies

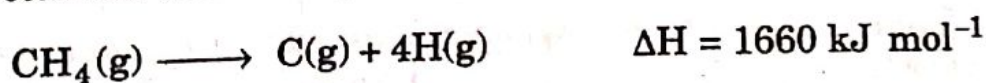
The energies required to break one mole of bonds in a substance in the gaseous state into atoms in the gaseous state is called bond energy. Energy is always required to break a chemical bond and is released when a bond is formed. The net energy that is released or absorbed in chemical reactions is due to the difference between the energies associated with the chemical bonds of the reactants and the products. The energy involved in a chemical reaction is known as *heat of reaction* and is measured in terms of enthalpy change, ΔH.

$$\Delta H_{reaction} = \Delta H_{products} - \Delta H_{reactants}$$

The bond energy is defined as enthalpy change (ΔH) when one mole of bonds is broken in the gaseous state". The SI units for bond energies are kilojoules per mole of bond (kJ/mol). Bond energies can be measured by calorimetry and spectroscopic methods. For example, for the reaction,

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = +436 \text{ kJ}$$

the bond energy of the H – H bond is 436 kJ/mole of bonds, which is called the bond **dissociation energy**.

Let us consider more complex molecules. For the reaction

$$CH_4(g) \longrightarrow C(g) + 4H(g) \qquad \Delta H = 1660 \text{ kJ mol}^{-1}$$

Since the four hydrogen atoms are identical, all the C – H bonds are identical in bond length and strength in methane molecule. However, the energies required to break the individual C–H bonds differ for successively broken bonds, as shown below.

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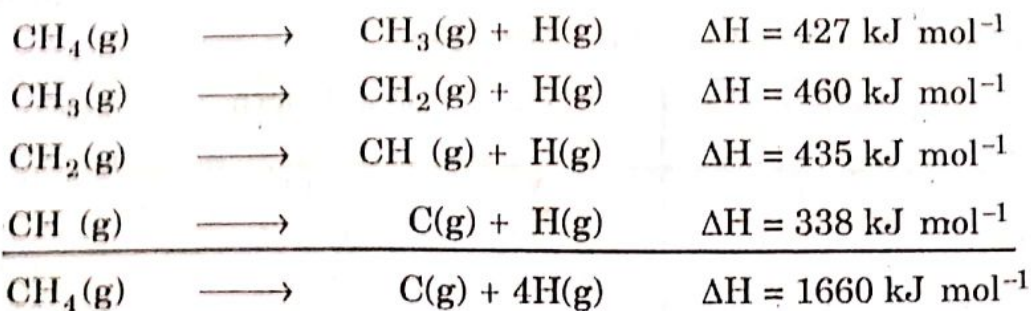
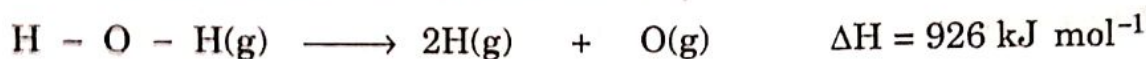
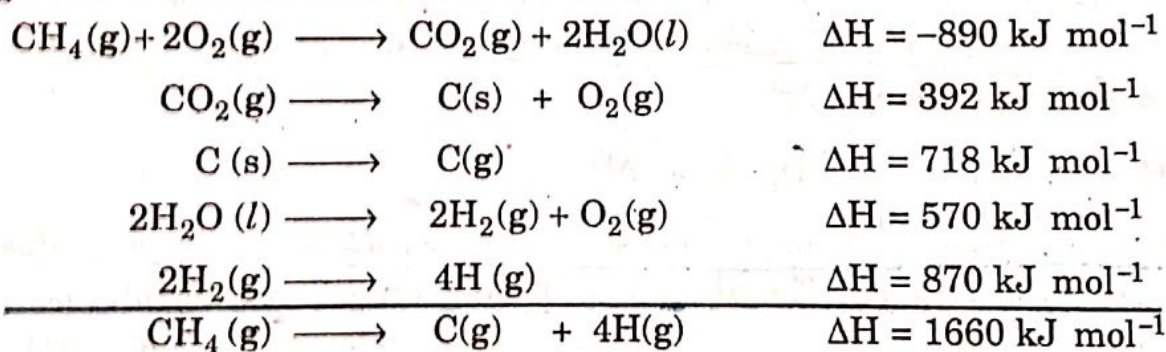
$$CH_4(g) \longrightarrow CH_3(g) + H(g) \qquad \Delta H = 427 \text{ kJ mol}^{-1}$$
$$CH_3(g) \longrightarrow CH_2(g) + H(g) \qquad \Delta H = 460 \text{ kJ mol}^{-1}$$
$$CH_2(g) \longrightarrow CH(g) + H(g) \qquad \Delta H = 435 \text{ kJ mol}^{-1}$$
$$CH(g) \longrightarrow C(g) + H(g) \qquad \Delta H = 338 \text{ kJ mol}^{-1}$$
$$CH_4(g) \longrightarrow C(g) + 4H(g) \qquad \Delta H = 1660 \text{ kJ mol}^{-1}$$

$$\text{Average C} - \text{H bond energy} = \frac{\Delta H}{4} = \frac{1660}{4} = 415 \text{ kJ mol}^{-1}$$

The average bond energy in methane is one fourth of the energy required to dissociate one mole of CH_4 into carbon and four hydrogen atoms. We do not try to measure the heat needed to break just one bond in a molecule with a number of bonds. Instead, we find the energy needed to break all of the bonds in the molecule and then divided by the number of bonds. This procedure gives us the average bond energy. We can define the average bond energy of the O – H bond in H_2O as follows:

$$H - O - H(g) \longrightarrow 2H(g) + O(g) \qquad \Delta H = 926 \text{ kJ mol}^{-1}$$

Since there are two O – H bonds, the average bond energy is

$$\Delta H/2 = 926/2 = 463 \text{ kJ/mol.}$$

The ΔH values may be determined from the heats of atomization of compounds. More commonly ΔH values are calculated from the heats of combustion, making use of the Hess's law, as shown below:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890 \text{ kJ mol}^{-1}$$
$$CO_2(g) \longrightarrow C(s) + O_2(g) \qquad \Delta H = 392 \text{ kJ mol}^{-1}$$
$$C(s) \longrightarrow C(g) \qquad \Delta H = 718 \text{ kJ mol}^{-1}$$
$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta H = 570 \text{ kJ mol}^{-1}$$
$$2H_2(g) \longrightarrow 4H(g) \qquad \Delta H = 870 \text{ kJ mol}^{-1}$$
$$CH_4(g) \longrightarrow C(g) + 4H(g) \qquad \Delta H = 1660 \text{ kJ mol}^{-1}$$

The average C – H bond energy is therefore 1660/4 = 415 kJ/mol at 25°C. Average values of bond energies for a number of different bond types are listed in table 2.1. Certain generalization can be derived from the bond energy data.

1. *There is a correlation between bond energy and bond distance. The stronger a chemical bond, the shorter the bond distance.*
2. *Bonds become weaker as we go down the periodic table, since bond distance increases as we go down the periodic table because the number of inner shells electrons increases.*
3. *A double bond is shorter and stronger than the corresponding single bond, and a triple bond, in turn, is shorter and stronger than the double bond.*

2.6 Ionic Character of Covalent Bonds (Polar and Nonpolar Covalent Bonds)

Covalent bonds are described as being either **polar** or ***nonpolar*** bonds. *"A covalent bond between two identical atoms like H-H or Cl-Cl, in which the bonding*

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electron pair is equally attracted by both the bonded atoms is called a **Nonpolar Covalent Bond".** In other words, in nonpolar covalent bonds the electron density is symmetrically distributed around the two nuclei in the molecular orbital. Thus, we can generalize, that the covalent bonds in all *homonuclear diatomic molecules* must be nonpolar. However, when a covalent bond exists between two atoms of different electronegativities, the atom with higher electronegativity attracts the bonding electron pair more strongly than the less electronegative atom. As a result, the atom with higher electronegativity acquires a partial negative charge (δ^-) and the less electronegative atom acquires a partial positive charge (δ^+). Such a bond which appears to have positive end and a negative end is called a **polar covalent bond** or **partially ionic covalent bond.** e.g., $H^{\delta+}-Cl^{\delta-}$, $H_3C^{\delta+}-Cl^{\delta-}$ "*A covalent bond between two unlike atoms in which there is an unsymmetrical distribution of electron density is called a* **polar bond.**" Consider, for example, the H – Cl bond. Since chlorine is more electronegative than hydrogen, the electron density in the molecular orbital would be higher around chlorine atom than around the hydrogen atom. Thus in the H – Cl molecule there will be a partial negative charge on chlorine and a partial positive charge on hydrogen. *"The power of an atom in a molecule to attract electrons to itself is called electronegativity."*

Polar covalent bonds may be thought of as being intermediate between pure (nonpolar) covalent bonds and pure ionic bonds. In fact, bond polarity is sometimes described in terms of *partial ionic character,* which usually increases with increasing difference in electronegativity between two bonded atoms. The amount of charge transferred from one atom to the other is a measure of the ionic character of the bond, and depends on the difference Δx between the electronegativity of the two atoms. If Δx is greater than about 2.0, the bond may be assumed to be almost ionic, e.g., Na^+Cl^-. If the electronegativity difference is less than 0.5, the amount of charge transferred is small and the bonding electrons are shared approximately equally between the two atoms. For intermediate values (0.5 to 2.0) of Δx, somewhat less than a full electronic charge is transferred, e.g., $H^{\delta+}-Cl^{\delta-}$, $H^{\delta+}-Br^{\delta-}$. The covalent bonds between H and Cl, H and Br are partially ionio covalent bonds.

The polarity of a bond tells us what kind of reactions can occur at the bond. Further the polarity of bond can make a molecule polar and thus affects its melting point, boiling point and solubility.

The electronegativity is related to ionization energy and electron affinity. The most widely used electronegative scale has been devised by Linus pauling from bond energies of diatomic molecules, which is based on the fact that the bond energy E_{A-B} between unlike atoms A–B is always greater than the arithematic mean of the bond energies E_{A-A} and E_{B-B}, because of the opposite partial charges on the two atoms of A–B bond, which attract each other and make the bond stronger, therefore, extra energy is required to break this A–B bond. The "extra" bond energy is directly

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proportional to the difference in electronegativities of the two bonded atoms, which is related to the ionic character of the bond. If the value of electronegativity of one element is arbitrarily fixed (which is assigned 4.0 to fluorine, the most electronegative element), the electronegativity of another element can be obtained by using the formula

$$X_A - X_B = \sqrt{\frac{\Delta}{96.5}}$$

Where X_A and X_B are the electronegativities of the elements A and B respectively, Δ is the difference between the bond energy E_{A-B} and the mean energies E_{A-A} and E_{B-B}, and 96.5 is an arbitrary constant. For example, Δ for H – Cl is

$$\Delta \text{ for HCl} = H_{H-Cl} - \frac{1}{2}(E_{H-H} + E_{Cl-Cl})$$

$$= 431 - \frac{1}{2}(435 + 243) = 92 \text{ kJ/mol}$$

$$X_{Cl} - X_H = \sqrt{\frac{92}{96.5}} = 0.988 = 0.99$$

$$X_{Cl} = X_H + 0.99 = 2.1 + 0.99 = 3.09$$

Electronegativities values of some elements are given in table 2.2

Table 2.2 Electronegativity of some elements on the pauling Scale

Elements	Electronegativity	Elements	Electronegativity
Na	0.9	N	3.0
K	0.8	P	2.1
Si	1.9	F	4.0
C	2.5	Cl	3.1
S	2.5	Br	2.8
H	2.1	I	2.5
O	3.5	Mg	1.2

2.7 Dipole Moment

The separation of charge in a polar covalent bond creates a **dipole.** The word dipole means "two poles" and refers to the positive and negative poles or ends, that result from the separation of charge within the molecule. The polarity of a molecule is expressed quantitatively by its **dipole moment,** μ (Greek letter mu), which is a measure of the magnitude of the separated charges and the distance between them. The **dipole moment,** μ, *is defined as the product of the magnitude of the charge, q, (at either end) and the distance, d, between the centres of gravity of the positive and negative charges.*

$$\mu = q \times d$$

The charges are of the order of 10^{-10} esu and distances are of the order of 10^{-8} cm; therefore, the usual magnitude of the dipole moment is of the order of

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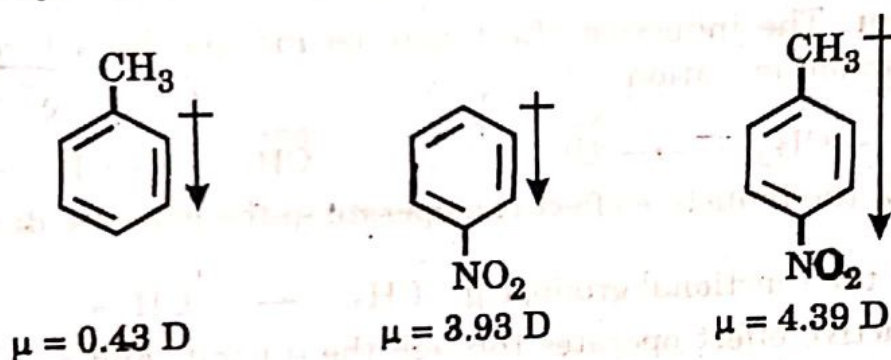
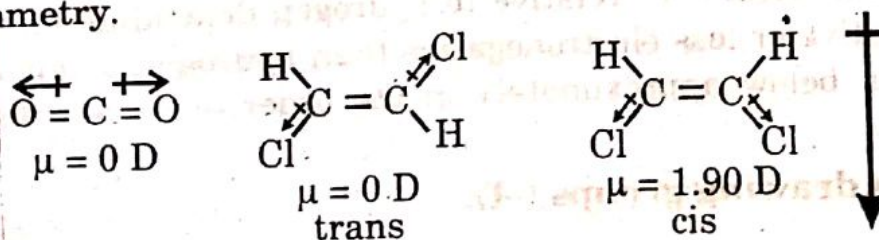
10^{-18} esu cm. For convenience this unit, 1×10^{-18} esu cm is defined as one **debye** and is abbreviated D. In SI units, dipole moments are measured in coulomb-meter (C.m). 1D = 3.34×10^{-30} C.m. However, commonly unit used is Debye, D. Thus CH_3Cl which has a dipole moment = 1.87D. It is not possible to determine the individual bond moments within a molecule; we can only measure the *net dipole moment of the molecule, which is a victorial sum of the individual bond moments which are directional.* The direction of the dipole moment is indicated by an arrow over a molecule pointing towards the negative pole. The values of the individual bond moments are roughly the same in all molecules, and therefore, can be used to calculate the expected dipole moments of the molecules. For example, the dipole moment of toluene is 0.43D and that of the nitrobenzene is 3.93D; the dipole moment of *p*-nitrotoluene is therefore expected to be 4.36 D. The actual value is 4.39D which is very close to the expected value.

CH_3 NO_2 CH_3 NO_2

μ = 0.43 D μ = 3.93 D μ = 4.39 D

Many molecules which have polar bonds do not exhibit dipole moment because the individual bond moments are so oriented that they cancel out one another. Any molecule that has a centre of symmetry do not exhibit dipole moment. For example, the bonds in the CO_2 molecule are polar, with dipoles directed towards the more electronegative O atoms. However, μ = 0 for CO_2 molecule because the molecule is linear and the two bond moments which are equal and in opposite direction cancel out each other. Similarly, trans-1, 2-dichloroethylene does not exhibit any dipole moment although its cis-isomer has a dipole moment of 1.90D, since in cis-isomer the bond moments are so oriented so as to provide overall electrical dissymmetry.

O = C = O H Cl C = C Cl H H H C = C Cl Cl

μ = 0 D μ = 0 D trans μ = 1.90 D cis

Similarly, the dipole moment of CCl_4, CH_4, *p*-dinitrobenzene, etc., is zero and these molecules are nonpolar. In general, the dipole moment is the measure of the polarity of the molecule. *The greater the value of the dipole moment, the greater the polarity of the molecule.*

2.8 Inductive Effect (I Effect) V.V. Imp.

The inductive effect of a group of atoms is the change in the electron density at

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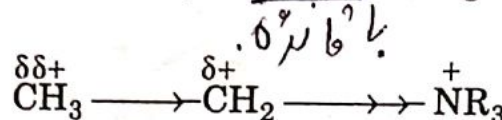
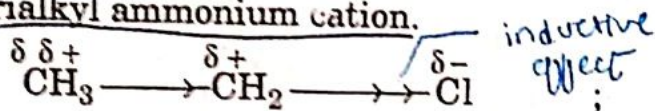
a nearby atom caused by differences in electronegativity. The inductive effect can be "electron-releasing" or "electron-withdrawing," meaning that the electron density at the nearby site is either increased or decreased, respectively.

Chlorine being more electronegative than carbon atom makes C–Cl bond in chloroethane polar, decreasing the electron density of the α-carbon atom and producing a partial positive charge on it. The α-carbon will attract the bonding electron pair between it and the β-carbon more to itself and thus creates a partial positive charge on the β-carbon, but the charge will be smaller than on C_α because the effect of Cl atom has been transmitted through C_α to C_β. The β-carbon, in turn, will attract the bonding electron pair between it and a β-hydrogen atom more to itself, creating a partial positive charge on the β-hydrogen. Thus a polar bond between two unlike atoms induces charge separation in an adjacent bond and even further along a chain. This permanent dipole induced by another is called the **inductive effect.** The inductive effect may be induced by a formal charge as in ethyltrialkyl ammonium cation.

$$\overset{\delta\delta+}{CH_3} \longrightarrow \overset{\delta+}{CH_2} \longrightarrow\!\!\!\rightarrow \overset{\delta-}{Cl} \quad ; \quad \overset{\delta\delta+}{CH_3} \longrightarrow \overset{\delta+}{CH_2} \longrightarrow\!\!\!\rightarrow \overset{+}{NR_3}$$

Similarly, the inductive effect can operate in the opposite direction depending on the nature of the functional group, e.g., $\overset{\delta\delta-}{CH_3} \longleftarrow \overset{\delta-}{CH_2} \longleftarrow\!\!\!\leftarrow O^-$.

The inductive effect operates through the σ bonds and can be considered as dipole-dipole and charge-dipole interactions. It is not confined to the polarization of one bond. It is transmitted through a chain of bond and the effect decreases with increasing chain length.

The polarization of a bond induced by an adjacent polar bond through movement of σ electrons is called **inductive effect**.

The inductive effect refers to the polarity produced in a molecule as a result of higher electronegativity of one atom compared to another.

The functional groups responsible for producing inductive effect can be classified as with an electron-withdrawing inductive effect (–I) or with an electron-donating inductive effect (+I), relative to hydrogen depending on whether they are more electronegative or less electronegative than hydrogen. Some of the common –I and +I are given below approximately in the order of decreasing strength of the inductive effects.

Electron – with drawing groups (–I):

$\overset{+}{N}R_3, \overset{+}{N}H_3, NO_2, CN, COOH, F, Cl, I, OAr, COOR, SH, OH, C\equiv CR, Ar, CH=CR_2$

Electron - donating (electron-releasing) **group (+I):**

$O^- > COO^- > R_3C > R_2CH > CH_3$

Alkyl groups have usually been regarded as electron-donating, but in recent years many examples have been found, and their behaviour in some cases is best explained by +I and –I in relative to hydrogen, depending on the situation.

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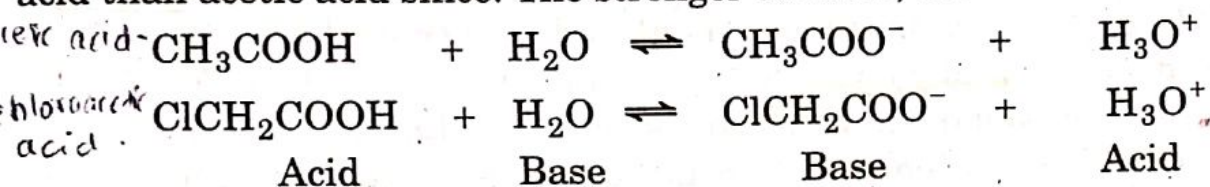
The inductive effect changes the electron density at the atoms involved and, therefore, their reactivity is affected. **Chloroacetic acid is about 100 times more acidic than acetic acid.** This can be explained by the fact that chlorine is electronegative and therefore exerts an electron-withdrawing inductive effect to disperse the electron density from the oxygens of COO^-. The anion $ClCH_2COO^-$ is therefore a weaker base than CH_3COO^-, and thus chloroacetic acid is a stronger acid than acetic acid since. The stronger the acid, the weaker is its conjugate base.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$\underset{\text{Acid}}{ClCH_2COOH} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Base}}{ClCH_2COO^-} + \underset{\text{Acid}}{H_3O^+}$$

Fluoroacetic acid is more stronger than chloroacetic acid: F is more electronegative than Cl and more effectively with draws electron density from the oxygens of COO^-. FCH_2COO^- is therefore a weaker base than $ClCH_2COO^-$ and, thus FCH_2COOH is a stronger acid than $ClCH_2COOH$. 3-chloropropanoic acid, $ClCH_2CH_2COOH$ is a weaker acid than chloroacetic acid; The inductive effect diminishes as the number of C's between Cl and the O's increases. $ClCH_2COO^-$ is a weaker base than $ClCH_2CH_2COO^-$. Thus chloropropanoic acid is weaker acid than chloroacetic acid.

On the other hand, the electron-donating group (+I) destablizes the carboxylate anion relative to the carboxylic acid and thus decreases its acidity. Acetic acid is 10 times less acidic than formic acid due to presence of methyl group which is regarded as electron-donating as compared to hydrogen.

Since basicity of the amines depends upon the availability of the unshared pair of electrons on the nitroge ., the electron repelling inductive effect of alkyl groups makes the primary and secondary amines more basic than ammonia. Although tertiary amines are more basic than ammonia, they are less basic than secondary (trimethyl amine, a tertiary amine; is the weakest unsubstituted aliphatic amine). This anomaly has been explained on the basis of salvation and the consequent stabilization of the conjugate acids of amines by water through hydrogen bonding. The conjugate acid of a tertiary amine has less capacity to enter into hydrogen bonding as compared to a secondary amine The third alkyl group, though increase the inductive effect, always mars the solvation tendency in tertiary amines. Since, the solvation becomes more effective than +I effect when comparing the pK_a values of conjugate acids of secondary and tertiary amines, the former are always stronger.

Conjugate acids	$\overset{+}{N}H_4$	$CH_3\overset{+}{N}H_3$	$(CH_3)_2\overset{+}{N}H_2$	$(CH_3)_3\overset{+}{N}H$
pK_a values	9.27	10.62	10.77	9.80

Another closely related effect to the inductive effect is known as the field effect. The inductive effect operates through the sigma (σ) bonds. Whereas the field effect operates directly through space or solvent molecules. Generally, the field effect

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depends on the geometry of the molecule but the inductive effect depends only on the nature of the bonds. It is very difficult to separate the inductive and field effects, they are frequently grouped together under the name of **field effect.**

2.9 Delocalized Chemical Bonding

A multiple covalent bond is formed by sharing of two or even three electron pairs between two atoms. *A covalent bond in which the electron density is concentrated between only two nuclei of the combining atoms is called* **localized bond** *and the bonding electrons are called* **localized electrons.** The compounds containing localized bonds are fully described by a single lewis structure. There are, however, many organic compounds in which one or more bonding orbitals are spread out more than two nuclei (i.e., atoms), the resulting bonds are called **delocalized bonds.** *Systems that have a p-orbital on an atom adjacent to a double bond (i.e., molecules with delocalized π bonds) are called* **conjugated unsaturated systems.** This phenomenon is called **conjugation.** In simple words, *the alternation of single and double (or triple) bonds in a molecule is referred to as conjugation.* The *p* orbital may be one that contains a single electron as in allyl radical, $CH_2=CH\dot{C}H_2$, it may be vacant *p* orbital as in allyl cation $CH_2=CH\overset{+}{C}H_2$, or it may be the *p* orbital of another double bond as in 1,3-butadiene, $CH_2=CH-CH=CH_2$. A conjugated system is not fully described by a single lewis structure. Conjugation gives these systems special properties. For example, conjugated radicals, ions, or molecules are more stable than nonconjugated ones. Conjugation also allows molecules to undergo unusual reactions.

The conjugated systems can be described either by the molecular orbital method or resonance method.

The Molecular orbital Method

In molecular orbital theory, the delocalized bond in conjugated systems are described in terms of delocalized molecular orbitals (*p* orbitals which are spread out more than two atoms). We shall demonstrate this with the allylic system and 1,3-butadiene.

1. Double bond in conjugation with a *p* orbital; Allylic System

The allylic system includes allyl radical, allyl cation. In the allyl radical, $CH_2=CH\dot{C}H_2$, each carbon is sp^2 hybridized (since each carbon is bonded to only three other atoms). The C – C σ bonds result from sp^2-sp^2 overlaps and the C–H σ bonds result from sp^2-s overlap. This leaves a *p* orbital on each carbon atom, each containing one electron. All carbon and hydrogen atoms lie in one plane and the *p* orbitals are parallel to each other and perpendicular to the plane of σ bonds. The central *p* orbital is in a position to overlap equally with both the terminal *p* orbitals. The three *p* orbitals of the allyl radical linearly combine to form three π molecular orbitals, i.e., a bonding, a nonbonding and an antibonding molecular orbitals (Fig. 2.25).

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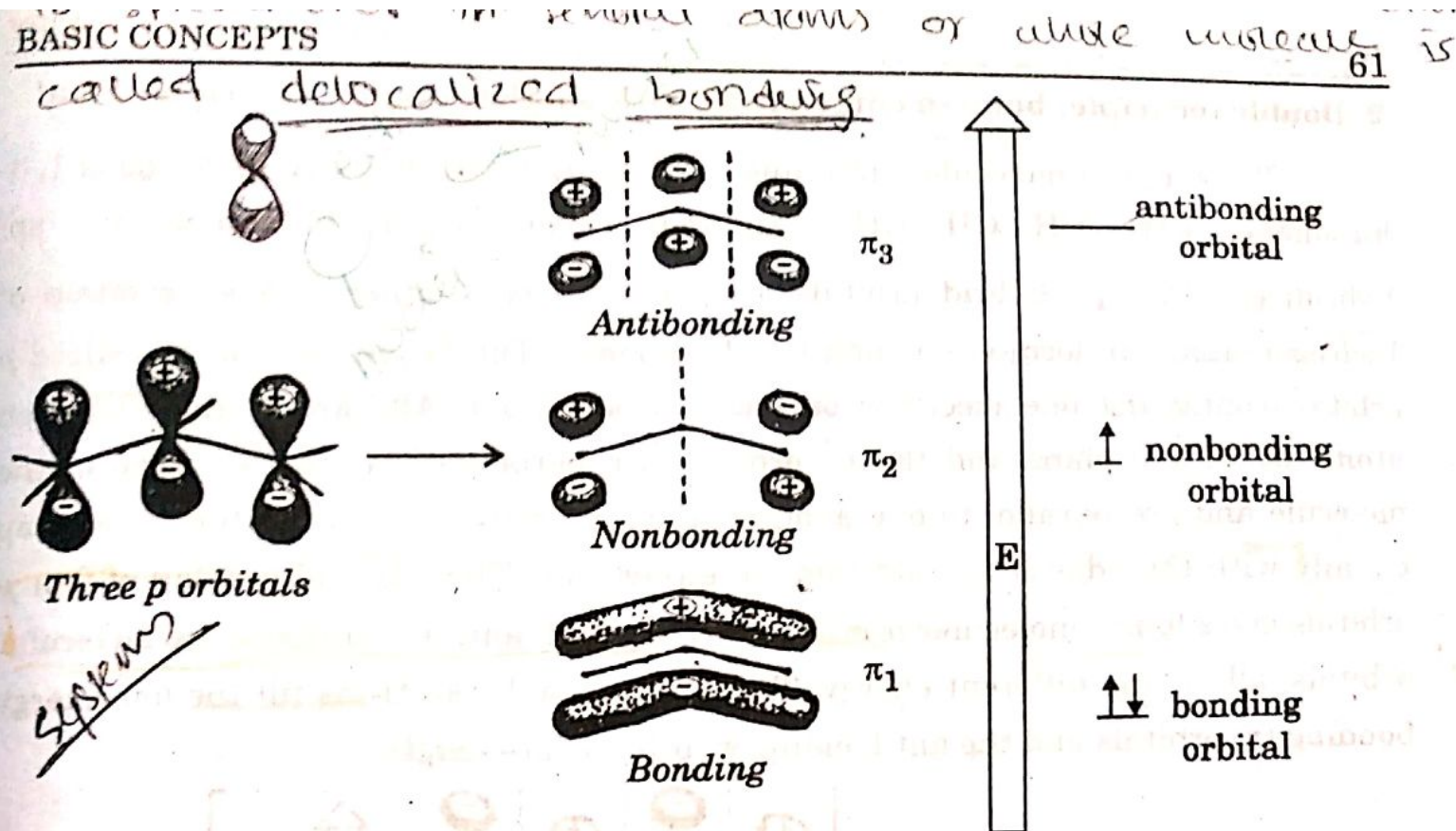
Fig. 2.20. The combination of three p orbitals to form three π MO in the allyl radical

The plane of the allyl molecule is a nodal plane for each molecular orbital which thus has two parts, one above and one below the plane and this is the node only in the bonding π molecular orbital. The bonding π molecular orbital is of lowest energy; it encompasses all three carbons and is occupied by two spin-paired electrons. The nonbonding π orbital is occupied by one unpaired electron and it has a node at the central carbon atom in addition to the nodal plane. This node means that the unpaired electron is found in the vicinity of carbon 1 and 3. The antibonding π* molecular orbital is of highest energy and is empty. It has two nodes–one between each pair of C atoms in addition to the nodal plane. Thus in the allyl radical three *p* orbitals overlap to form a set of molecular orbitals that encompass all three carbons. The unpaired electron of the allyl radical and the two electrons of the π bond are delocalized over all three carbons and the allyl radical is said to be a *conjugated unsaturated system*. This delocalization of the unpaired electron accounts for the greater stability of the allyl radical as compared to primary, secondary, and tertiary radicals.

The **allyl cation,** $CH_2 = CH\dot{C}H_2$ has molecular picture similar to allyl radical, but only two *p* electrons are available and these will occupy the lowest energy bonding molecular orbital. The nonbonding and antibonding π* molecular orbitals will remain empty. Since the π electrons are attracted by three nuclei rather than only two (as in the case of localized π orbital), the allylic carbocation has special stability.

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2. Double (or triple) bond in conjugation with another double (or triple) bond

The simplest molecule containing a conjugated system of double bonds is 1, 3-butadiene, $CH_2 = CH - CH = CH_2$. All four cabons in 1,3-butadiene are sp^2 hybridized. The sp^2 hybrid orbitals overlap with each other and s orbitals of hydrogen atoms to form C – C and C – H σ bonds. This leaves one unhybridized p orbital (containing one electron) on each carbon atom. All carbon and hydrogen atoms lie in one plane and the p orbitals are perpendicular to the plane of the molecule and are parallel to one another. Each p orbital is in a position to overlap equally with the adjacent p orbitals on either side. This mutual overlap of four p orbitals gives four π molecular orbitals – two bonding and two antibonding molecular orbitals, all having different energy. The four available electrons fill the low energy bonding (π) orbitals and the antibonding π* orbitals are empty.
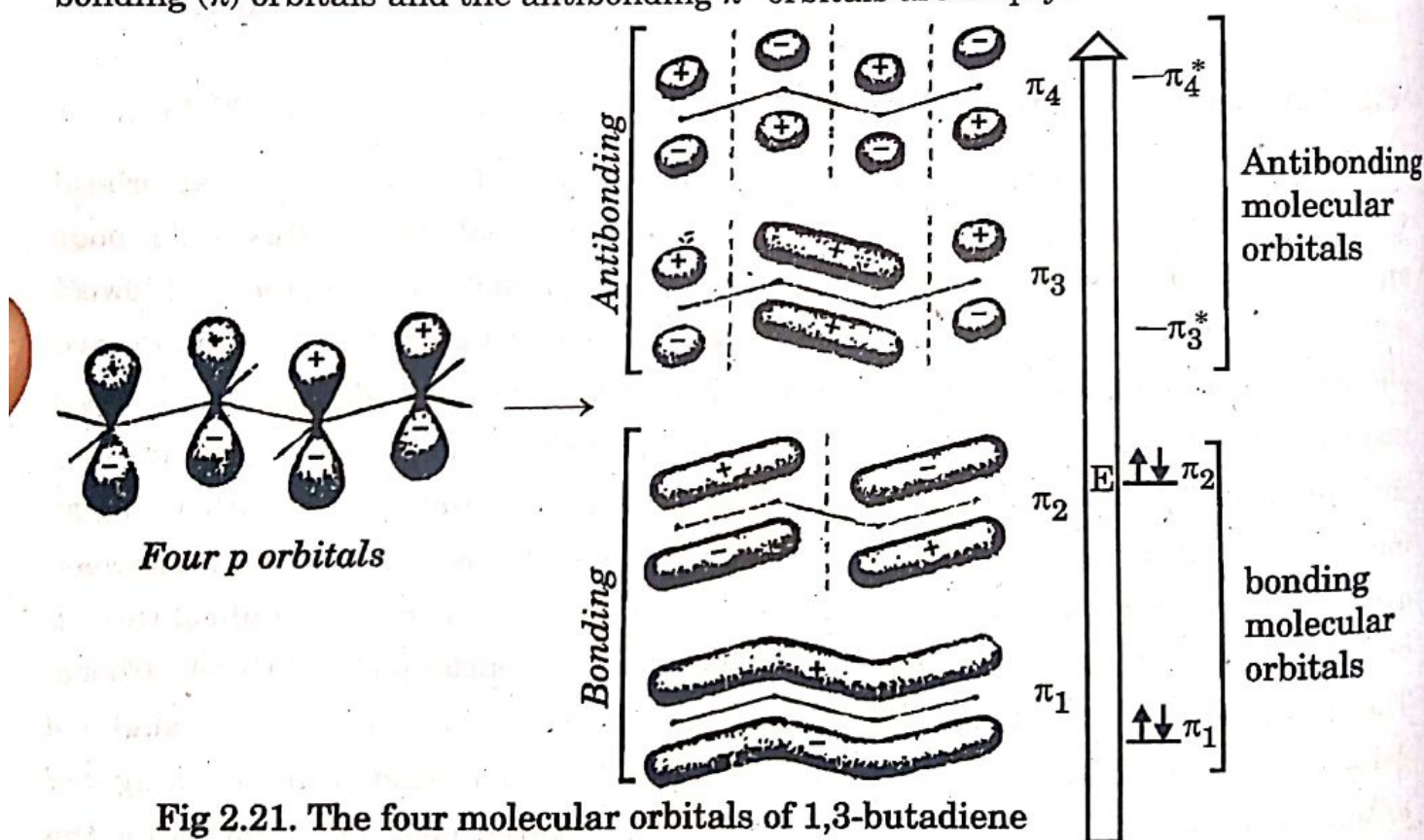
Fig 2.21. The four molecular orbitals of 1,3-butadiene

The plane of the molecule is a nodal plane for each molecular orbital. Note that as we go from π_1, (bonding) to π_4^* (antibonding), each orbital has one more node than the one of next lower energy. In general, when p orbitals overlap, as in butadiene, they do so in such a way as to produce one molecular orbital having no node, a second molecular orbital with one node, a third with two nodes, and a fourth with three nodes. These nodes are in addition to the nodal plane. The relative energy of the molecular orbitals depends on the number of nodes; the greater the number of nodes, the higher the energy of the molecular orbital. The conjugated dienes are

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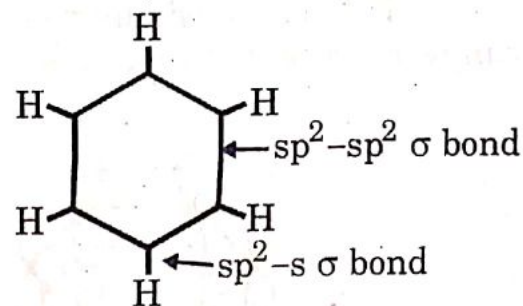
more stable than isolated dienes. The extra stability arises from the additional delocalization of the π electrons that occurs in conjugated dienes.

Benzene

Since each carbon atom in the benzene is bonded to three other atoms, i.e., two carbons and one hydrogen, the six carbon atoms in benzene are sp^2 hybridized. The sp^2 hybrid orbitals overlap with each other and with 1*s* orbitals of the six hydrogen atoms forming C – C and C–H σ bonds. There remains one unhybridized *p* orbital containing one electron on each carbon atom. Each *p* orbital is in a perfect position to overlap with the neighbouring *p* orbitals on either side.

Linear combination of six *p* orbitals gives six pi (π) molecular orbitals – three bonding and three antibonding molecular orbitals.

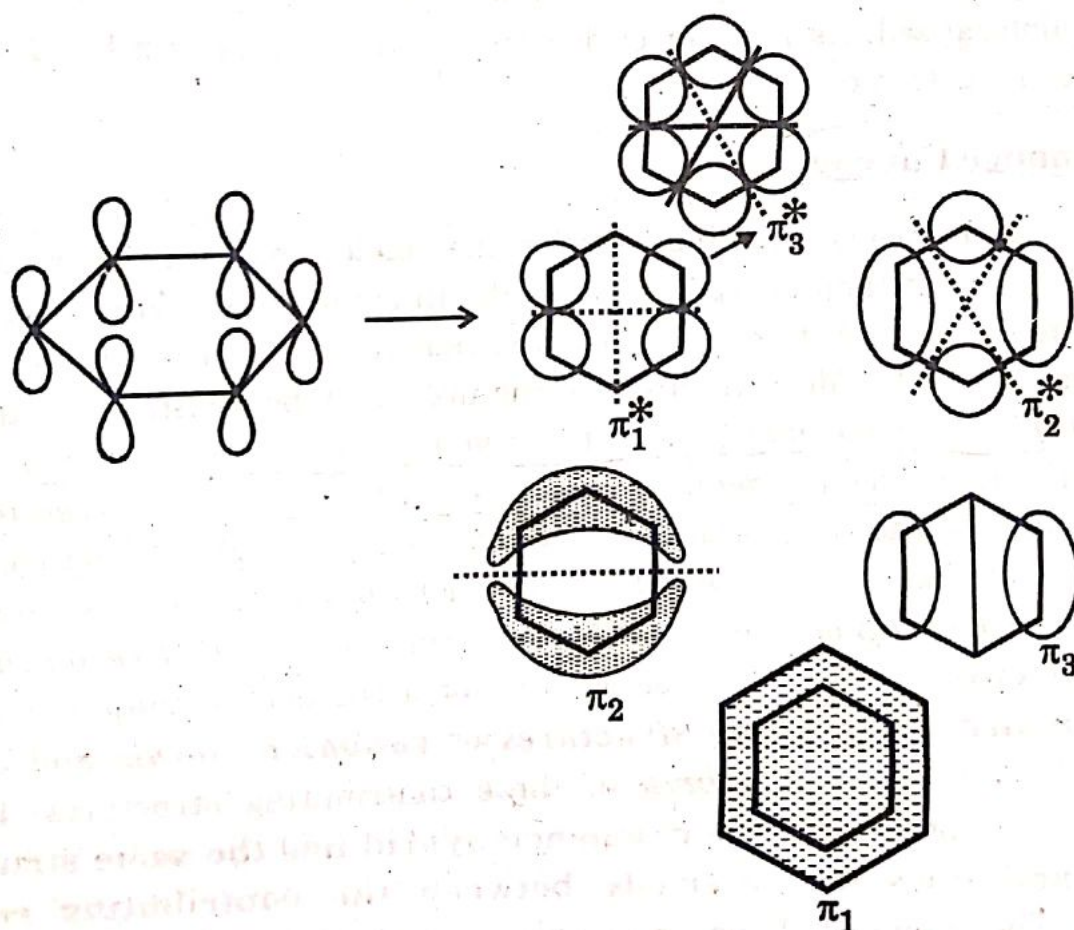



Fig. 2.22. Six π molecular orbitals of benzene, formed by the overlap of six 2p orbital

The six available electrons fill the three lowest energy bonding orbitals, π_1, π_2 and π_3, while the three antibonding orbitals, π_1^*, π_2^* and π_3^* remain empty when the benzene is in the ground state (most stable state).

The most stable bonding orbitals, π_1 has no node. It concentrates electron

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density between each pair of nuclei. The bonding orbitals π_2 and π_3 are of equal energy, each having one node. Similarly, the two antibonding orbitals π_1^* and π_2^* are of equal energy each having two nodes. The least stable antibonding orbital, π_3^* has three nodes between the nuclei.

The combined effect of six electrons in π_1, π_2 and π_3 orbitals in benzene ring can be represented as a cloud of electrons above and below the ring as shown in Fig.
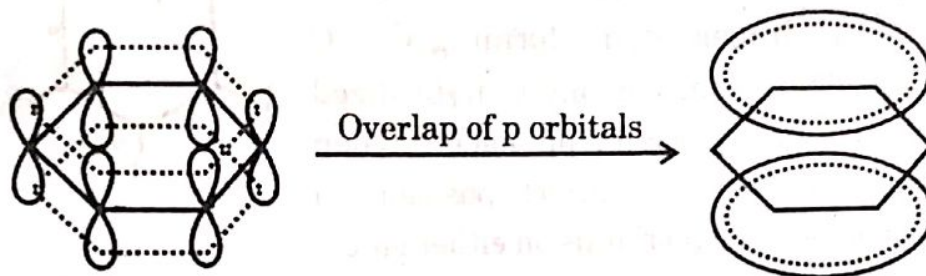
Fig. 2.23 Combined effect of bonding orbitals in benzene

The six electrons of the *p* orbitals now cover all the six carbon atoms and are said to be delocalized. As a result of delocalization, a stronger π bond and a more stable molecule is formed.

2.10 Resonance Concept

Resonance theory describes species (i.e. molecules, ions or radicals) with delocalized electrons (and charges) in π bonds. In a compound where there is more than one reasonable location for a multiple bond, no *single* lewis structure can describe the molecule. More than one structure must be written for an accurate description. *The phenomenon in which two or more lewis structures can be written for a compound which involve identical positions of atoms, is called* ***resonance***. The actual structure of the compound is considered to be a weighted average of all the contributing structures. *The representation of a real structure of a compound as a weighted average of two or more contributing structures is called* ***resonance***. When two or more lewis structures can be written for a compound, these structures are called ***resonance contributing structures*** or ***canonical forms*** and the actual structure is a ***resonance hybrid*** of these contributing structures. It is very important to recongnize that the **resonance hybrid has the same structure all the time and does not alternate between the contributing resonance structures.** The resonance hybrid resembles to each of the contributing structures but identical non of them. A double headed arrow ($\longleftrightarrow$) is placed between each pair of contributing structures to represent the resonance hybrid. The double headed arrow does not mean the oscillation of molecule from one lewis structure to another. Rather, it means that the real structure is a blend of the contributing structures, which are imaginary. For example, the various contributing structures of benzene are:

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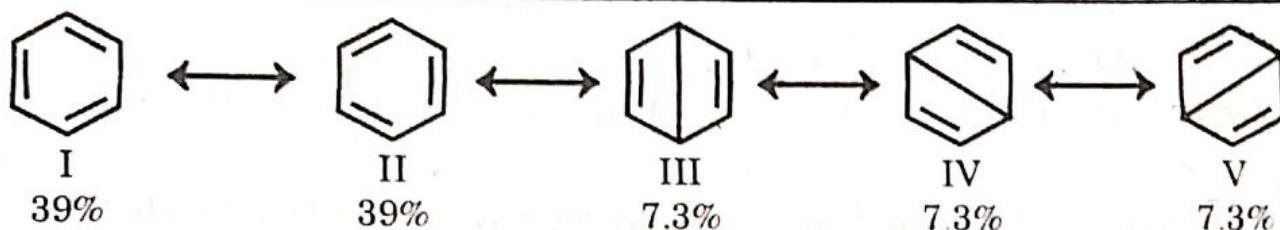

None of these structures represent benzene satisfactory. The real structure of benzene is a resonance hybrid of two Kekule structures (I and II) and three Dewar structures (III, IV and V). The Kekule structures I and II, each contribute 39% and Dewar structures, III, IV and V, contribute 7.3% each to the actual molecule. Obviously, the two Kekule structures contribute largely to the resonance hybrid, hence benzene is a resonance hybrid, principally, of two Kekule structures.

We have seen, it is not necessary that the actual molecule should resemble each contributing structure to the same extent. The actual molecule (hybrid) may resemble one contributing structure more than it does another, since the hybrid has lower energy than any of the contributing structures, and it will resemble those contributing structures more closely which have lower energy.

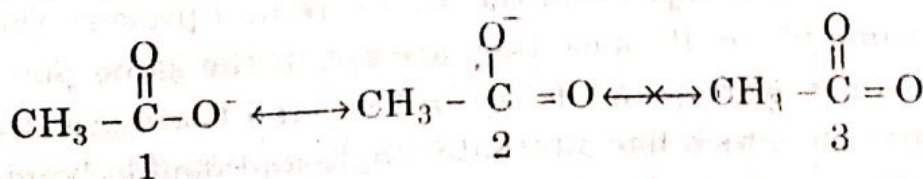
The energy of the actual molecule, the resonance hybrid, is always less than the calculated energy of any hypothetical contributing structure. *The difference in energy between the resonance hybrid and the contributing structures of the lowest energy is called* **resonance (delocalization) energy.**

The Rules of Resonance

The rules for writing resonance structures, which contribute to a resonance hybrid are as follows:

1. Resonance structures are not actual structures for the molecule. *They are nonexistent, hypothetical and exist only on paper. Resonance structures are useful because they allow us to describe molecules, radicals and ions for which a single Lewis structure is inadequate.*

2. All the contributing structures must be bonafide lewis structures. For instance, in any canonical form the maximum number of covalent bonds that an atom may have is one for hydrogen, two for halogens, three for oxygen, four for carbon and four for nitrogen. Also note that when the oxygen atom bears a unit negative charge it has one covalent bond, when oxygen atom is electrically neutral it has two bonds and when oxygen atom has a unit positive charge, it has three bonds. For example,

$$\underset{1}{CH_3-\overset{\overset{O}{\|}}{C}-O^-} \longleftrightarrow \underset{2}{CH_3-\overset{\overset{O^-}{|}}{C}=O} \longleftrightarrow\!\!\!\!\!\!\times\;\; \underset{3}{CH_3-\overset{\overset{O}{\|}}{C}=O}$$

Structure 3 is not a proper resonance structure because carbon has five covalent bonds.

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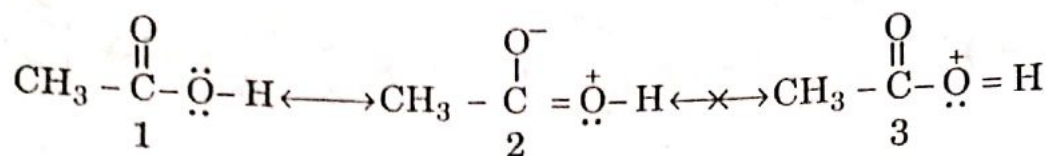
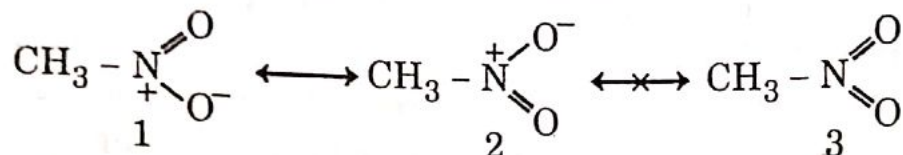
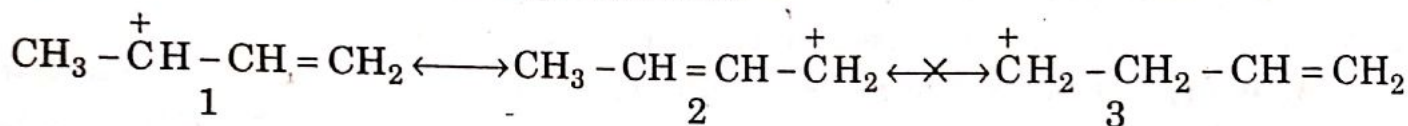
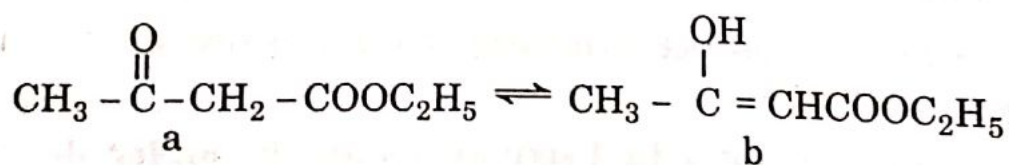
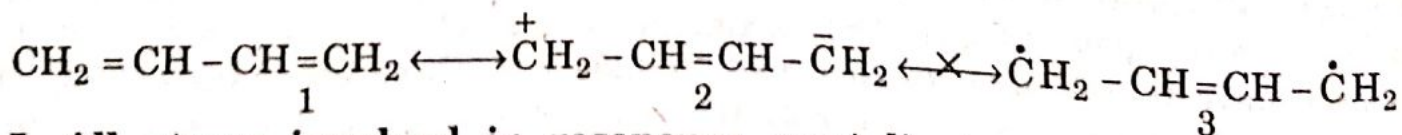
$$\underset{1}{CH_3-\overset{O}{\overset{\|}{C}}-\ddot{\underset{..}{O}}-H} \longleftrightarrow \underset{2}{CH_3-\overset{O^-}{\overset{|}{C}}=\overset{+}{\underset{..}{O}}-H} \longleftrightarrow\!\!\!\!\!\!\times\;\; \underset{3}{CH_3-\overset{O}{\overset{\|}{C}}-\overset{+}{\underset{..}{O}}=H}$$

Structure 3 is not valid because hydrogen has two covalent bonds.

Again consider the resonance picture of a nitro compound: Here structure 3 is not valid because nitrogen has five covalent bonds. Note that when nitrogen bears a unit positive charge, it has four covalent bonds.

$$\underset{1}{CH_3-\overset{+}{N}(=O)-O^-} \longleftrightarrow \underset{2}{CH_3-\overset{+}{N}(-O^-)=O} \longleftrightarrow\!\!\!\!\!\!\times\;\; \underset{3}{CH_3-N(=O)=O}$$

3. In writing resonance structures we are only allowed to move electrons. The atomic nuclei must have the same positions in all the canonical forms. Structure 3 below is not a resonance structure for the allylic cation because the position of hydrogen atom has been changed (moved).

$$\underset{1}{CH_3-\overset{+}{C}H-CH=CH_2} \longleftrightarrow \underset{2}{CH_3-CH=CH-\overset{+}{C}H_2} \longleftrightarrow\!\!\!\!\!\!\times\;\; \underset{3}{\overset{+}{C}H_2-CH_2-CH=CH_2}$$

The two forms of acetoacetic ester represent two different compounds which are in equilibrium with each other; they are not the canonical forms of the same compound as the position of a hydrogen has changed in going from a to b.

$$\underset{a}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOC_2H_5} \rightleftharpoons \underset{b}{CH_3-\overset{OH}{\overset{|}{C}}=CHCOOC_2H_5}$$

4. All canonical forms must have the same number of unpaired electrons. The structure 3 below is not a resonance structure for the 1,3-butadiene because it has two unpaired electrons while the canonical forms of butadiene have no unpaired electrons.

$$\underset{1}{CH_2=CH-CH=CH_2} \longleftrightarrow \underset{2}{\overset{+}{C}H_2-CH=CH-\overset{-}{C}H_2} \longleftrightarrow\!\!\!\!\!\!\times\;\; \underset{3}{\dot{C}H_2-CH=CH-\dot{C}H_2}$$

5. All atoms involved in resonance must lie in a plane. The reason for planarity is to allow maximum overlap of the *p* orbitals for the delocalization of the electrons. For example, 2, 3-di-tert-butylbutadiene behaves like a *nonconjugated* diene because the large tertbutyl groups twist the structure and prevent the double bonds from lying in the same plane. Because they are not in the same plane, the *p* orbitals at C–2 and C–3 do not overlap and delocalization (and therefore resonance) is prevented. Cyclooctatetraene which has alternate single and double bonds, but it does not show resonance because its molecule is not planar but tub-shaped as shown below.

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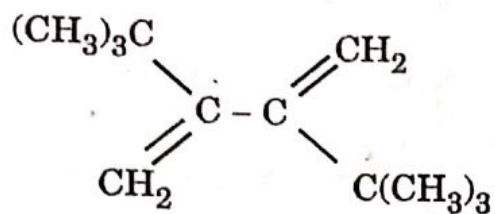
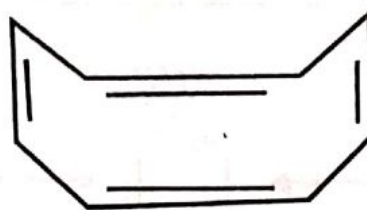
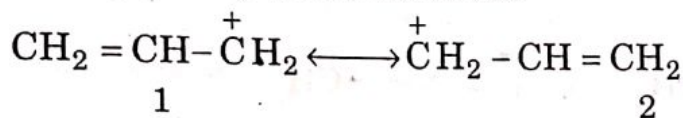
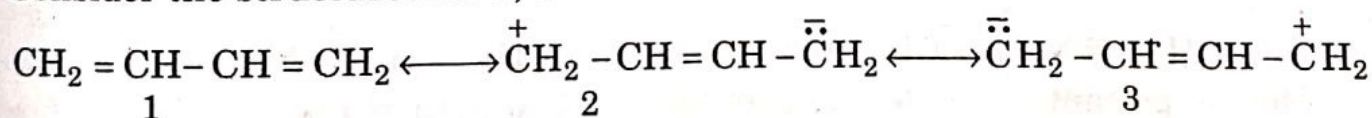
$$(CH_3)_3C(C{=}CH_2)-C(=CH_2)C(CH_3)_3$$

2, 3-di-tert-butylbutadiene

Cyclooctatetraene

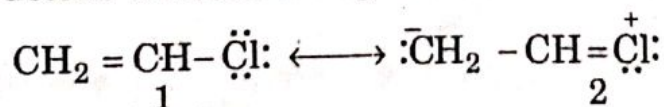
6. The actual molecule, i.e. the resonance hybrid, is always more stable than any of its canonical forms. This is because in any one canonical form each pair of bonding electrons is localized only between two atoms, whereas in the resonance hybrid the π electrons are delocalized over three or more atoms. The delocalization of π electrons accounts for the extra stability of the hybrid. Resonance, therefore, is a stabilizing phenomenon and the hybrid is said to be resonance stabilized. The actual allyl cation, for example, is more stable than either canonical form 1 or 2 taken separately would indicate.

$$\underset{1}{CH_2=CH-\overset{+}{C}H_2} \longleftrightarrow \underset{2}{\overset{+}{C}H_2-CH=CH_2}$$

Contribution of resonance structures:

7.All resonance structures do not contribute equally to the actual molecule. Each structure contributes in proportion to its stability. The more the stability of a resonance structure, the more is its contribution. It is not always easy to decide the relative stabilities of resonance structures. However, the following rules may be helpful in making decision about the relative stabilities of resonance structures.

(a) Structures with more covalent bonds are generally more stable than with fewer. Consider the structures for 1, 3-butadiene.

$$\underset{1}{CH_2=CH-CH=CH_2} \longleftrightarrow \underset{2}{\overset{+}{C}H_2-CH=CH-\overset{\cdot\cdot}{\bar{C}}H_2} \longleftrightarrow \underset{3}{\overset{\cdot\cdot}{\bar{C}}H_2-CH=CH-\overset{+}{C}H_2}$$

The structure 1 is the most stable and the most important contributor because it contains more covalent bonds.

(b) Structures without a charge are more stable than those with charge separation. Separating opposite charges require energy. Charge separation decreases stability, especially, if charge separation leads to reduction in the number of covalent bonds. If structures with separated charges have the same number of covalent bonds as those without a charge, their contribution is significant. For example, for vinyl chloride below structure 1 makes a larger contribution because it does not have separated charges and structure 2 makes a significant contribution because it has separated charges. A structure without charges means that there is no charge separation.

$$\underset{1}{CH_2=CH-\ddot{C}l:} \longleftrightarrow \underset{2}{:\bar{C}H_2-CH=\overset{+}{C}l:}$$

major contribution   significant contribution

$$H_3C-\ddot{O}-CH=CH_2 \longleftrightarrow H_3C-\overset{+}{O}=CH-{}^{-}CH_2$$

major contribution   significant contribution

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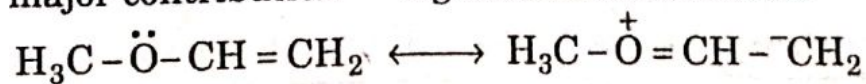
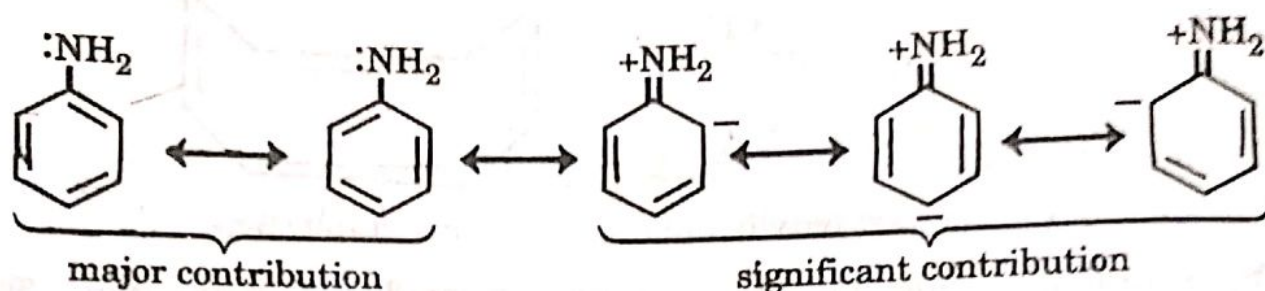
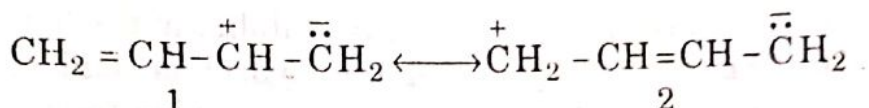
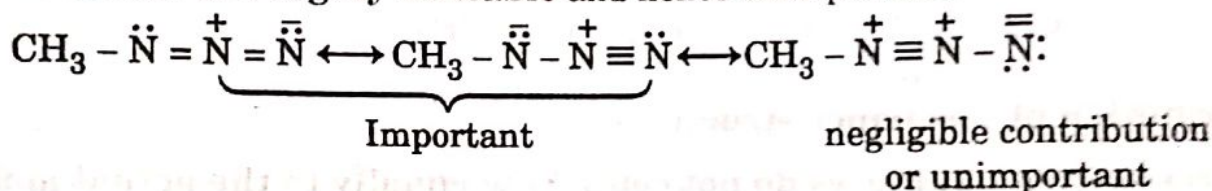
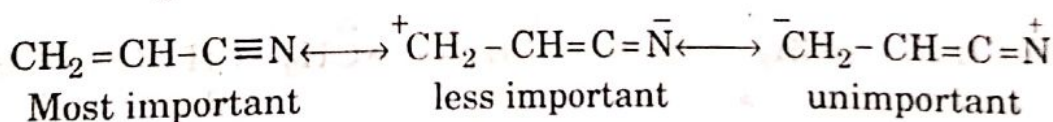
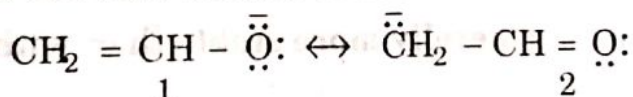
$:NH_2$ (benzene ring) ⟷ $:NH_2$ (benzene ring) ⟷ $^+NH_2$ (ring, −) ⟷ $^+NH_2$ (ring, −) ⟷ $^+NH_2$ (ring, −)

major contribution — significant contribution

(c) The greater the charge separation, the less the stability. Structure 2 is less stable than 1.

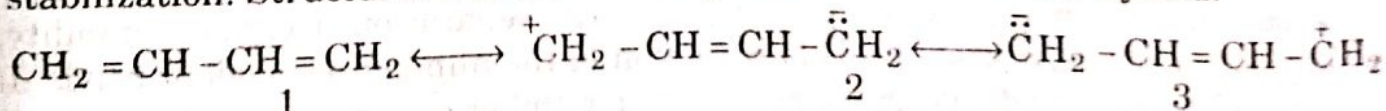
$$\underset{1}{CH_2=CH-\overset{+}{C}H-\overset{..}{\bar{C}}H_2} \longleftrightarrow \underset{2}{\overset{+}{C}H_2-CH=CH-\overset{..}{\bar{C}}H_2}$$

(d) Resonance structures with like charges on the same atom or on adjacent atoms are highly unstable and hence unimportant.

$$CH_3-\ddot{N}=\overset{+}{N}=\overset{..}{\bar{N}} \longleftrightarrow CH_3-\overset{..}{\bar{N}}-\overset{+}{N}\equiv\ddot{N} \longleftrightarrow CH_3-\overset{+}{N}\equiv\overset{+}{N}-\overset{=}{\underset{..}{N}}:$$

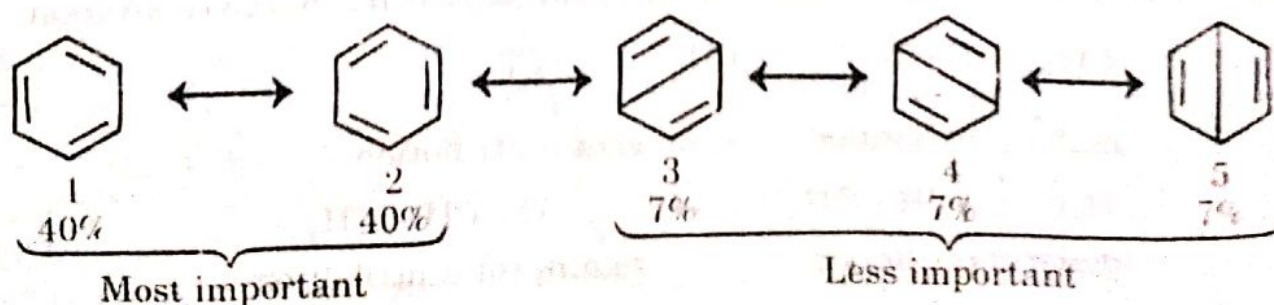
Important — negligible contribution or unimportant

(e) Structure with a negative charge on a more electronegative atom are more stable than those in which the negative charge is on a less electronegative atom. Thus structure 1 is more stable than 2. Similarly, positive charges are best carried on atoms of low electronegativity.

$$\underset{1}{CH_2=CH-\overset{..}{\underset{..}{\bar{O}}}:} \leftrightarrow \underset{2}{\overset{..}{\bar{C}}H_2-CH=\underset{..}{O}:}$$

$$\underset{\text{Most important}}{CH_2=CH-C\equiv N} \longleftrightarrow \underset{\text{less important}}{\overset{+}{C}H_2-CH=C=\bar{N}} \longleftrightarrow \underset{\text{unimportant}}{\bar{C}H_2-CH=C=\overset{+}{N}}$$

(f) Equivalent resonance structures make equal contribution to the resonance hybrid, and the system described by them have a large resonance stabilization. Structures 2 and 3 make equal contribution to the hybrid.

$$\underset{1}{CH_2=CH-CH=CH_2} \longleftrightarrow \underset{2}{\overset{+}{C}H_2-CH=CH-\overset{..}{\bar{C}}H_2} \longleftrightarrow \underset{3}{\overset{..}{\bar{C}}H_2-CH=CH-\overset{+}{C}H_2}$$

(g) Structures in which bond angles and bond length resemble closely with the resonance hybrid are more stable than those with distorted bond angles and bond lengths, e.g.,

1 (40%) ⟷ 2 (40%) ⟷ 3 (7%) ⟷ 4 (7%) ⟷ 5 (7%)

Most important (1, 2) — Less important (3, 4, 5)

Structures 1 and 2 are of equal energy but 3, 4 and 5 have one bond each which is longer than a normal covalent bond and therefore, are less important.

(h) The greater the number of principal contributing structures of a molecule the greater the stability, especially if the contributing structures are of equal energy. For example, the nitrate ion is more stable than the nitrite ion:

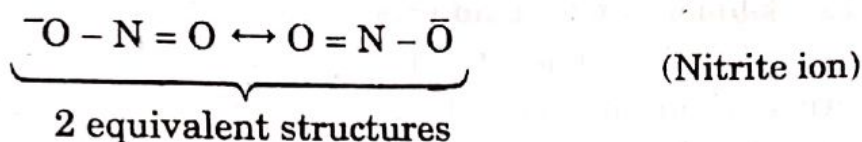
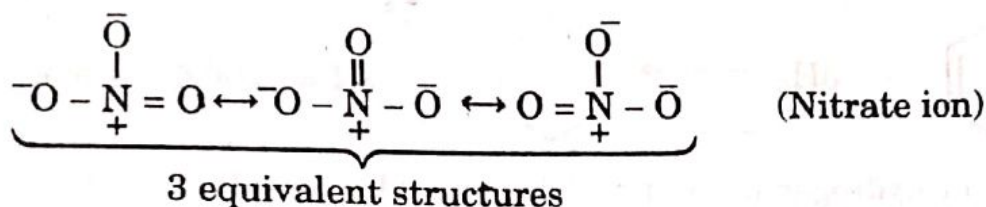
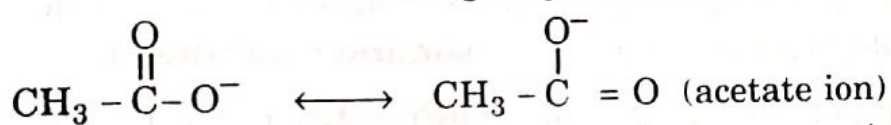
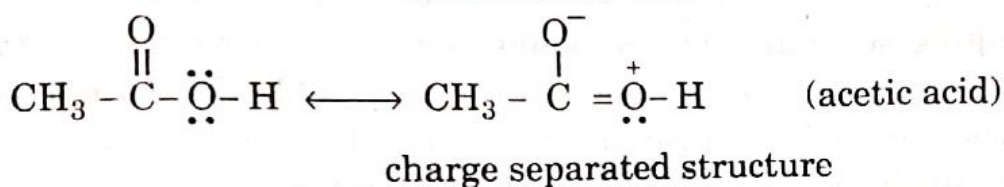
$$\underbrace{{}^{-}O-\overset{\overset{\bar{O}}{|}}{\underset{+}{N}}=O \leftrightarrow {}^{-}O-\overset{\overset{O}{\|}}{\underset{+}{N}}-\bar{O} \leftrightarrow O=\overset{\overset{O^{-}}{|}}{\underset{+}{N}}-\bar{O}}_{\text{3 equivalent structures}} \quad \text{(Nitrate ion)}$$

$$\underbrace{{}^{-}O-N=O \leftrightarrow O=N-\bar{O}}_{\text{2 equivalent structures}} \quad \text{(Nitrite ion)}$$

Acetate ion is more stable than acetic acid

$$CH_3-\overset{\overset{O}{\|}}{C}-\ddot{O}-H \longleftrightarrow CH_3-\overset{\overset{O^{-}}{|}}{C}=\overset{+}{\ddot{O}}-H \quad \text{(acetic acid)}$$

charge separated structure

$$CH_3-\overset{\overset{O}{\|}}{C}-O^{-} \longleftrightarrow CH_3-\overset{\overset{O^{-}}{|}}{C}=O \quad \text{(acetate ion)}$$

Two equivalent structures without charge separation.

In acetic acid, one resonance structure is with charge separation and makes less contribution to the resonance hybrid than the other without charge separation. On the other hand, both the resonance structures of acetate ion are equivalent and thus make equal contribution to the resonance hybrid. Therefore, acetate ion is more stable than acetic acid. That is why acetic acid readily loses a proton to form a more stable anion and thus behaves as an acid.

2.11 RESONANCE ENERGY

The energy of the actual molecule (hybrid) is always less than the calculated energy of any hypothetical contributing structure. *The difference in energy between the most stable contributing structure and the actual molecule (the hybrid) is called the* **resonance energy** (sometimes called the **stabilization energy** or **delocalization energy**). The resonance energy can never be measured, only estimated, since we can measure the energy of the actual molecule practically but the energy of the contributing structure can only be estimated from its bond energies by comparison with an arbitrarily chosen model compounds, since contributing structure does not exist. One method frequently used for estimation of resonance energy involves measurements of **heats of hydrogenation.** For example, the resonance energy of benzene can be estimated by comparing heats of hydrogenation

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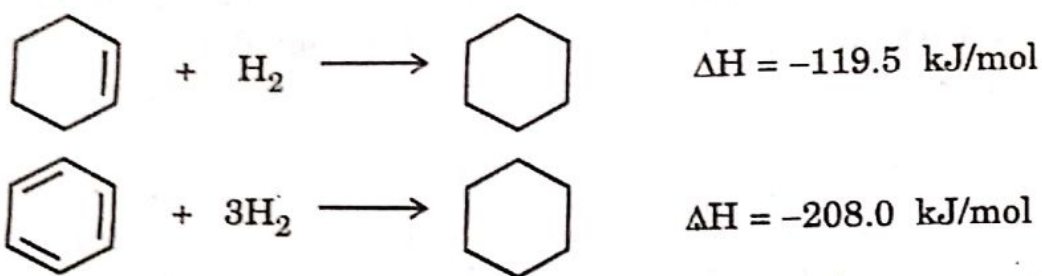
of benzene with that of cyclohexene. In both the cases the same product, cyclohexane is obtained.

$$\text{Cyclohexene} + H_2 \longrightarrow \text{Cyclohexane} \qquad \Delta H = -119.5\ \text{kJ/mol}$$

$$\text{Benzene} + 3H_2 \longrightarrow \text{Cyclohexane} \qquad \Delta H = -208.0\ \text{kJ/mol}$$

The heat of hydrogenation of cyclohexene which contains one carbon-carbon double bond is 119.5 kJ/mol. If we would expect the most stable resonance structure of benzene is simply 1,3, 5-cyclohexatriene (hypothetically), we would expect the heat of hydrogenation of benzene to be 119.5 × 3 = 358.5kJ/mol, which is three times that of cyclohexene. The observed value of the heat of hydrogenation of benzene is 208kJ/mol, which is less (358.5–208 = 150.5kJ/mol) than the expected value of the most stable contributing structure. The resonance energy of benzene, therefore, is 150.5kJ/mol. Thus the real molecule of benzene is more stable than a hypothetical 1, 3, 5-cyclohexatriene (i.e., Kekule structure). In short all compounds which cannot be described by a single Lewis structure but a combination of contributing structures have extra stability and are said to be **resonance stabilized.**

The more nearly equal in energy the contributing structures, the greater the resonance energy and the less the hybrid looks like the contributing structures. When contributing structures have dissimilar energies, the hybrid looks like the lowest-energy structure. The resonance energy increases as the number of the principal contributing structures increases. For example the resonance energy of benzene, naphthalene, anthracene and phenanthrene, for which we can draw two, three, four and five principal contributing structures, respectively, is 150.0, 255.0, 351.0 and 384.5 kJ/mol.

2.12 Resonance Effect

The resonance (or mesomeric) effect refers to the polarity produced in a molecule as a result of interaction between two π bonds or a π bond and lone pair of electrons. This effect operates *through π electrons of double and triple bonds and is transmitted along a chain of carbon atoms.* The resonance effect is of great importance in conjugated compounds. In such systems, the π electrons get delocalized as a result of resonance effect giving a number of resonance structures of the molecule.

The distribution of electron density in a system involving resonance is not the same as it would be if there were no resonance. For example, *aniline, $C_6H_5NH_2$, an aromatic amine, is a weaker base than ammonia or aliphatic amine,* because in aniline the electrons density due to unshared electron pair of nitrogen is delocalized over to the ring, resulting in the decrease of electron density on the nitrogen atom

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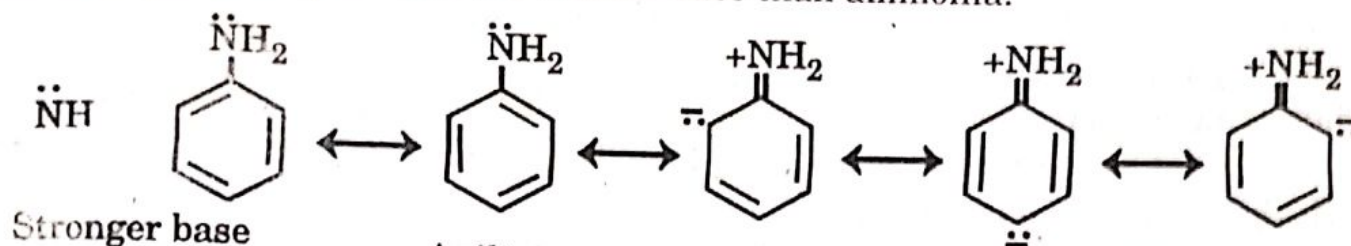
and the corresponding increase of electron density on the ring due to resonance effect while in ammonia or aliphatic amines, *where the resonance is absent,* the unshared electrons pair resides entirely on the nitrogen atom. The decreased electron density on the nitrogen atom of aniline relative to ammonia or aliphatic amines explains why aniline is a weaker base than ammonia.

$\ddot{N}H$ Stronger base

Aniline, a weaker base due to resonance effect.

The decrease in electron density at one position accompanied by a corresponding increase at another position in conjugated compounds is called ***resonance effect.*** The resonance effect like the inductive effect may be positive or negative. Atoms or groups which donate electrons towards a carbon atom are said to have a **+M effect.** Those atoms or groups which draw electrons away from a carbon atom are said to have **–M effect.**

In general, a group containing an unshared electron pair on an atom connected to an unsaturated system, donates an electron pair to the unsaturated system by the resonance effect is said to be **electron-donating (+M group).** A group containing a multiple bond, involving an electronegative atom, connected to an unsaturated system, withdraws electrons from the unsaturated system by the resoanance effect is said to be electron-withdrawing **(–M group).** Some common atoms or groups which cause +M or –M effect are listed below:

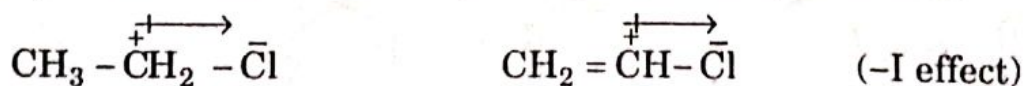
Electron-donating groups (+M effect groups):

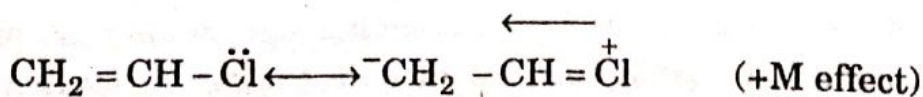
$-Cl, -Br, -I, -NH_2, -OH, -OR, -OCOR, O^-$, Ar

Electron-withdrawing groups (–M groups):

$-NO_2, -CN, -COOH, -COOR, -CONH_2, -CHO, -COR, -CONHR$, Ar

The group Ar is capable of both kinds of effect. The reoanance effect has an appreciable influence on the physical characteristics and chemical reactivities of resonance hybrids relative to molecule with no resonance. Consider, for example, **the dipole moment of vinyl chloride is smaller than that of ethyl chloride.** The C – Cl bond is polarized because the chlorine atom is electron with-drawing due to the inductive effect both in vinyl chloride and ethyl chloride.

$CH_3-\overset{+}{C}H_2-\overset{-}{Cl}$ $\quad$ $CH_2=\overset{+}{C}H-\overset{-}{Cl}$ $\quad$ (–I effect)

However, the molecule of vinyl chloride is a hybrid of resonance structures such as

$CH_2=CH-\ddot{Cl} \longleftrightarrow {}^{-}CH_2-CH=\overset{+}{Cl}$ $\quad$ (+M effect)

The chlorine atom is electron-donating due to resonance effect in the

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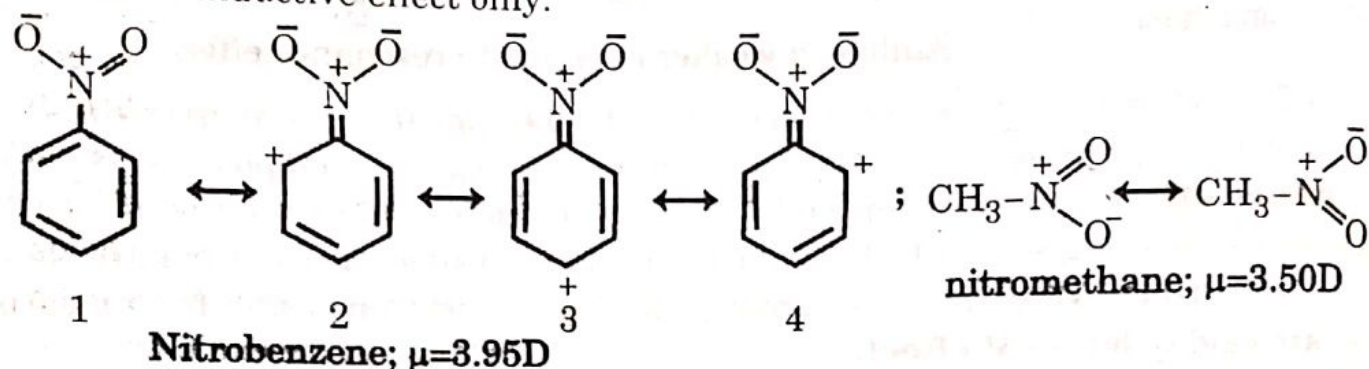
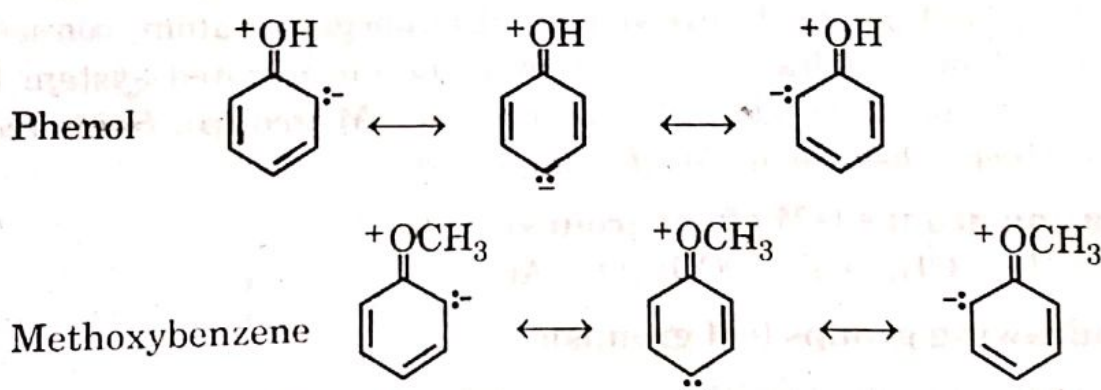
opposite direction in the contributing structure $^{-}CH_2 - CH = \overset{+}{Cl}$ to the inductive effect. The resonance effect is absent in ethyl chloride. Since the resonance effect is opposed to the inductive effect in this case, therefore, the observed dipole moment of vinyl chloride is smaller than that ethyl chloride. The larger dipole moment of nitrobenzene (μ=3.95D) is due to the contribution of structure, 2,3 and 4 which have greater separation of charges. The nitro group in nitrobenzene is, thus electron-withdrawing inductively as well as by resonance. The two effects combined together increase the dipole moment of nitrobenzene relative to nitromethane (μ = 3.50 D) which shows inductive effect only.

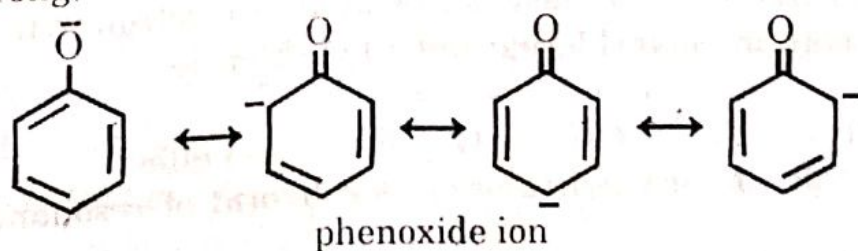
1 ⟷ 2 ⟷ 3 ⟷ 4 ; $CH_3-\overset{+}{N}(=O)O^- \longleftrightarrow CH_3-\overset{+}{N}(O^-)=O$

nitromethane; μ=3.50D

Nitrobenzene; μ=3.95D

Similarly the dipole moments of aniline, phenol, chlorobenzene and methoxy benezene are smaller than those of their aliphatic analogues due to significant contributions of their resonance contributing structures.

Phenol ^{+}OH ⟷ ^{+}OH ⟷ ^{+}OH

Methoxybenzene $^{+}OCH_3$ ⟷ $^{+}OCH_3$ ⟷ $^{+}OCH_3$

The greater acidity of phenols relative to alcohols can be attributed to resonance stabilization through delocalization of the negative charge of phenolate anion over the benzene ring, while the negative charge on the alkoxides anion, RO^- cannot be delocalized. Phenoxide ion is therefore a weaker base than RO^-, and phenol is a stronger acid.

phenoxide ion

The influence of nitro group in further increasing the acidity of phenol, particularly in the ortho and para positions, because it further delocalizes the negative charge over to the nitro group, increasing the number of resonance

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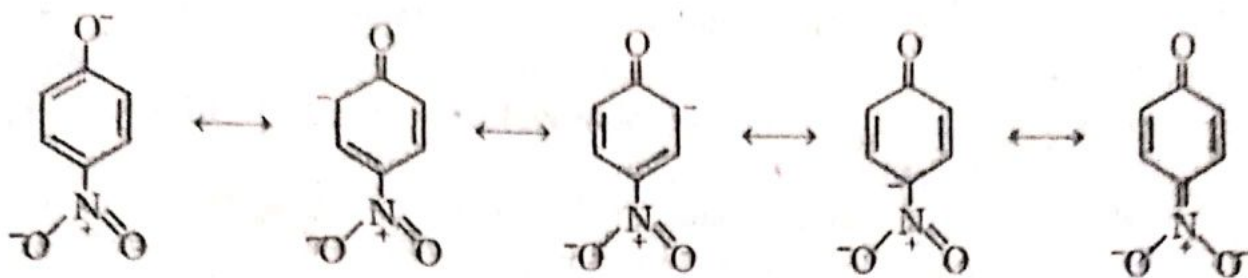
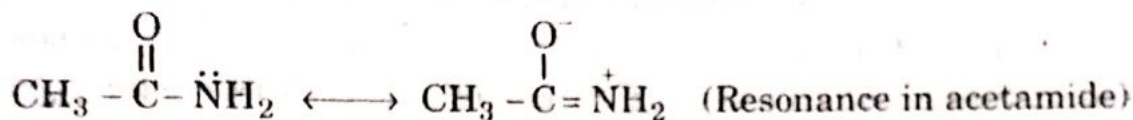
contributing structures.

The basicity of amines is very sensitive to resonance effects as is shown above that aniline is a weaker base than the aliphatic amines. Nitro group further reduces the basicity of aromatic amines which results from dispersal of the unshared pair of electrons on nitrogen into the nitro group in addition to the resonance seen in aniline.

Amides are much less basic than amines, largely because of delocalization of electrons of nitrogen, into carbonyl as shown below:

$$CH_3-\overset{\overset{\large O}{\|}}{C}-\ddot{N}H_2 \longleftrightarrow CH_3-\overset{\overset{\large O^-}{|}}{C}=\overset{+}{N}H_2 \quad \text{(Resonance in acetamide)}$$

The C-Cl bond length in vinyl chloride is shorter than that in CH_3CH_2Cl (ethyl chloride) due to resonance effect. The contribution of the structure $\bar{C}H_2-CH=\overset{+}{C}l$ shows greater electron density between carbon and Cl than expected from one bonding electron pair only (as in CH_3-CH_2-Cl). The increased electron density between C and Cl atoms in vinyl chloride enables them to come closer, therefore the observed C-Cl bond length in vinyl chloride is shorter than that in CH_3-CH_2-Cl.

Mostly the resonance effect is observed alongwith the field effect. The field effect operates through space or solvent molecules and depend on the geometry of the molecule, and it is difficult to separate the two effects. These are, therefore, frequently grouped together under the heading of **electrical effect.**

2.13 Steric Effect and its Applications

Destabilization resulting from van der Waals repulsion of groups that are close to each other is referred to as a **steric effect.** In other words, *the presence of group or atoms in close proximity of each other causes van der Waal repulsions and the phenomenon is called* **steric effect** (also known as **steric hindrance**). The steric effect in a reaction is ascribed to the difference in steric energy between, on the one hand, reactants and, on the other hand, a *transition state* (or products). A steric effect on a rate process may result in a rate increase ('steric acceleration') or a decrease ('steric retardation'). Steric effect largely depends upon the size (bulkiness) of the group or atom and arises from their arrangement in reacting species. Steric effects arise from contributions ascribed to *strain* as the sum of (i) non-bonded

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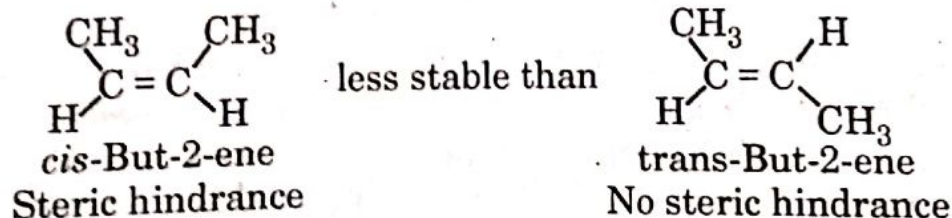
repulsions, (ii) bond angle strain and (iii) bond stretches or compressions. Some authors make a distinction between 'steric' effects attributed to van der Waals repulsions alone, and 'strain' effects attributed to deviations of bond angles from 'ideal' values.

This effect has a marked impact on the rate of reaction, its nature and the extent to which a reaction proceeds under a given set of conditions. Even if the reaction conditions are favourable there may be a change or inhibition of reaction due to steric effect. The stability of molecules, their chemical reactivity and few of the physical properties (like acidity and basicity) are greatly influenced by steric effect.

Stability of two geometric isomers. The relative stability of two geometric isomers is usually determined simply by considerations of **steric hindrance.** Trans-alkene is more stable than isomeric cis-alkene. In cis-alkenes, steric hindrance is present, as the alkyl groups are present on the same side of the double bond. Due to steric crowding, repulsive forces (van der Waals repulsion) occur between the groups and decrease the stability of cis-alkene as compared to trans-alkene. On the other hand, in trans-alkene, the alkyl groups are present on opposite sides of the double bond and repulsion does not occur. Thus *cis*-2-butene is slightly less stable than *trans*-2-butene, while with the bulkier phenyl groups the difference in energy between *cis*- and *trans*- stilbene (1,2-diphenylethylene) is so great that an equilibrium mixture contains 10^4 times as much trans as cis isomer at room temperature.

$$\underset{\text{Steric hindrance}}{\underset{\textit{cis}\text{-But-2-ene}}{(CH_3)(H)C=C(CH_3)(H)}} \quad \text{less stable than} \quad \underset{\text{No steric hindrance}}{\underset{\text{trans-But-2-ene}}{(CH_3)(H)C=C(H)(CH_3)}}$$

Because of higher stability, the heat of hydrogenation of trans-alkene is lesser than that of cis-alkene.

Hydrolysis of a haloalkane. Hydrolysis of a haloalkane is a nucleophilic substitution reaction that results in the formation of alcohol. In general, 1° haloalkanes follow S_N2 reactions whereas 3° haloalkanes follow S_N1 mechanism. Neopentyl bromide is a 1° haloalkane but the tert butyl group causes steric hindrance in the transition state of S_N2 mechanism and inhibits it from following a S_N2 mechanism during hydrolysis. However, the reaction may follow S_N1 mechanism during which it undergoes a carbocation rearrangement (1,2-methyl shift) to form more stable 3° carbocation that undergoes nucleophilic attack of water to form a 3° alcohol. Thus, although neopentyl bromide is a primary haloalkane but it hydrolysis does not follow S_N2 mechanism.

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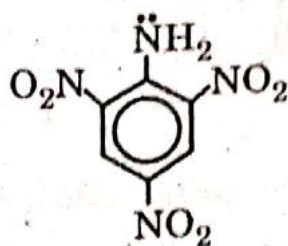
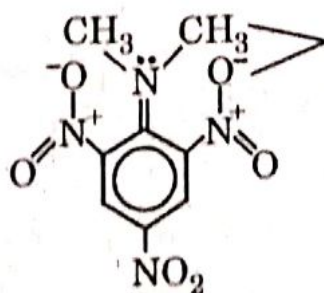
Effect of steric hindrance on Nucleophilicity. Because a proton is very small, basicity is relativity unaffected by steric hindrance. On the other hand, steric hindrance greatly affects the rate at which a transition state is reached in a bimolecular nucleophilic substitution (S_N2) reaction. For example, tert-butoxide ion is a much stronger base (by a factor of over 100) than methoxide ion, the later is a better nucleophile because it is less sterically hindred.

Acidity of Alcohols. The acidity of alcohols decreases as the degree of substitution of the carbinol carbon increases. Thus, in the solution-phase, acidities of methanol, ethanol, 2-propanol, and tert-butanol decrease by more than two pK_a units as the carbon bearing the OH group becomes more fully alkylated. However, the order of acidity in solution ($CH_3OH > C_2H_5OH >$ 2-propanol > tert-butanol), where solvation and intermolecular association are important, is reversed in the gas phase, where isolated molecules are observed. The pK_a in solution must therefore be sensitive to intermolecular effects. The replacement of a hydrogen atom by a group of comparable electronegativity, but much larger size, stabilizes an ion in the gas phase but induce a permanent destabilizing steric effect on the solvation of the same anion (conjugate base). The presence of alkyl substitutents on the carbinol carbon pushes the solvent molecules away from the negatively charged oxygen atom of the alkoxide and thus inhibits the stabilizing interaction of the solvent with the anion.

Basicity of Amines. The presence of three alkyl groups (+ I effect) in 3° amines increases the electron density on nitrogen but the crowding due to the presence of three bulkier groups hinders the ability of nitrogen to make these electrons available to other species (like solvent molecules). Thus the steric hindrance in 3 amines makes them less basic compared to 2° amines. Thus in aqueous solution the order of basicity is $(CH_3)_2NH > CH_3NH_2 < (CH_3)_3N$.

In general, the steric hindrance in 3° amines reduces the basicity as compared to 1° and 2° amines. However, in some cases, the steric hindrance enhances the basicity. For example, despite of steric crowding, N, N-dimethyl-2,4, 6-trinitroaniline is a much stronger base compared to 2,4,6-trinitroaniline.

NH_2, O_2N, NO_2, NO_2

2,4,6-trinitroaniline

CH_3 CH_3 — Steric hinderance inhibits the coplararity thus, –R effect due to nitro groups at ortho' position is not oserved.

N,N-Dimethyl 2,4,6-trinitroaniline

Steric Effects on Solvation. Steric hindrance to solvation caused by the bulk of the acid or of the solvent can inhibit solvent stabilization of the conjugate base.

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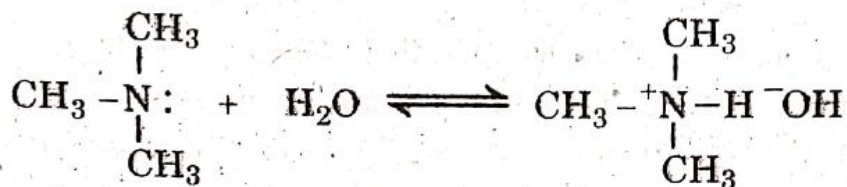
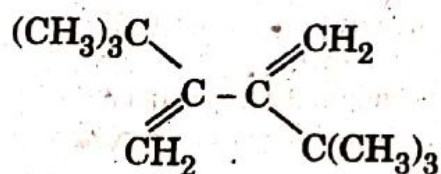
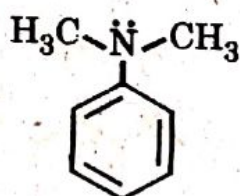
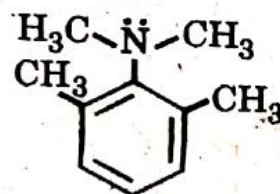
Acidity is thereby lowered.

Amines exhibit a similar steric inhibition of solvation. The order of base strength for methylamines in water is : $(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 > (CH_3)_3\ddot{N}$. In this series, solvent stabilization is more important for the conjugate acids, the charged species, than for the amines. Trimethylammonium ion is sterically the most hindered conjugate acid and therefore its stabilization by solvent is least effective.

$$(CH_3)_3N: + H_2O \rightleftharpoons (CH_3)_3\overset{+}{N}-H \ {}^{-}OH$$

$(CH_3)_2\ddot{N}H$ and $CH_3\ddot{N}H_2$ in the series are opposite in order to what would be predicted from steric considerations. Here both steric and inductive effects play a role. Inductive electron donation by methyl groups enhances electron density on the N atom and thus increases basicity. The basicity of dimethyl amine benefits more from the electron donating effect of two methyl groups than it loses from steric inhibition of solvation, thus it is more basic than methylamine. However, the order of the same series of amines in the gas phase is $(CH_3)_3\ddot{N} > (CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2$, that would be predicted from inductive effects in the absence of solvation.

Steric Inhibition of Resonance

According to one of the rules of resonance *all the atoms involved in resonance must lie in the same plane to facilitate delocalization of electrons.* The reason for planarity is maximum overlap of the *p* orbitals. Any structural feature that destroys this coplanarity of the conjugated system inhibits resonance. Many examples are known where resonance is prevented or reduced because the atoms are sterically forced out of planarity. For example, 2,3-di-tert-butylbutadiene behaves like a *nonconjugated* diene because the large tert-butyl groups twist the structure and prevent the double bonds from lying in the same plane. Because the double bonds are not in the same plane, the *p* orbitals at C–2 and C–3 do not overlap and delocalization (and therefore resonance) is prevented. This phenomenon is called **steric inhibition of resonance.**

$(CH_3)_3C$, CH_2, C – C, CH_2, $C(CH_3)_3$ — H_3C–$\ddot{N}$–CH_3 — H_3C–$\ddot{N}$–CH_3, CH_3, CH_3

2, 3- di.- tert - butylbutadiene **N, N - dimethylaniline** **2, 6, N, N - tetramethylaniline**

Consider, the effect of ortho substituents on the basicity of N, N-dimethylaniline which is less basic than aliphatic amines due to the delocalization of nonbonding electrons of the amino nitrogen atom over to the benzene ring mainly to

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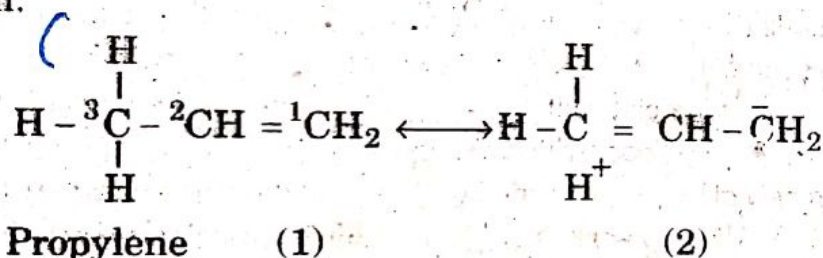
the ortho and para positions, dimethylamino group being coplanar with the benzene ring. However, substitution of methyl groups at the ortho positions pushes the dimethylamino out of the plane of the ring, making resonance delocalization of nonbonding electrons of the amino nitrogen atom impossible (diffuclt) and results in the increased basicity of 2, 6, N, N-tetramethylaniline as compared to N, N-dimethylaniline. This hindrance to delocalization by the methl groups in the ortho position by pushing the dimethylamino group out of the plane of the ring is called **steric inhibition of resonance.**

2.14 Hyperconjugation

We have discussed so far the delocalization of π electrons. There is another type of delocalization, called **hyperconjugation,** which involves σ electrons. *Hyperconjugation may be regarded as a $\sigma - \pi$ orbital overlap, analogous to the $\pi - \pi$ orbital overlap.* In hyperconjugation the sigma C–H bond on the alpha C is delocalized with the empty *p* orbital of a C = C or a carbocation. The resulting H^+ does not change its position. For compounds which have a CH, a CH_2, or a CH_3 group attached to an unsaturated carbon atom, canonical forms such as (2) can be written:

$$H-{}^{3}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-{}^{2}CH={}^{1}CH_2 \longleftrightarrow H-\underset{H^+}{\overset{\overset{H}{|}}{C}}=CH-\bar{C}H_2$$

Propylene (1) (2)

In the canonical form (2) there is no bond between the carbon and the hydrogen atoms. *This type of resonance is called* ***no bond resonance,*** and this system of conjugation where the σ electrons of a C–H bond are in conjugation with π electrons of the unsaturated system or with *p* orbital, is known as **hyperconjugation.**

The hydrogen atom does not leave the molecule (because 2 does not exist but is only a canonical form that contributes to the actual structure of the molecule). The effect of 2 is that in the resonance hybrid (actual molecule) the C–H bond under consideration is weaker than a normal C–H bond or it has character between a single and no bond and the bond between C_2 and C_3 has some double bond character and thus is expected to be shorter than an ordinary C–C single bond. For example, the observed CH_3-C bond length in propyne is 0.147 nm which is shorter than the normal C–C single bond length (0.154 nm). This can be explained by a partial double bond character developed due to hyperconjugation as shown in canonical form 2. $CH_3-C\equiv CH \longleftrightarrow \overset{+}{H}CH_2=C=\bar{C}H$

The more hyperconjugation structures that can be written for a species, the more stable is the species. Thus tertiary carbonium ion is more stable than a secondary carbonium ion which is more stable than a primary carbonium ion as

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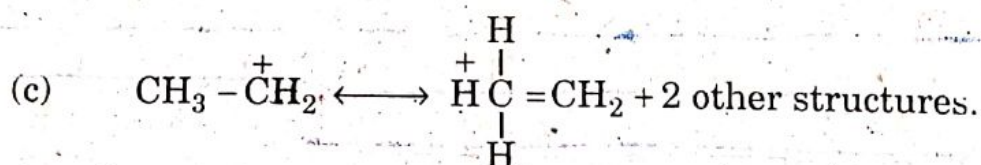
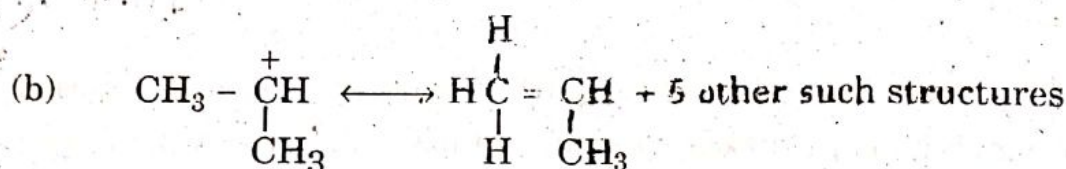
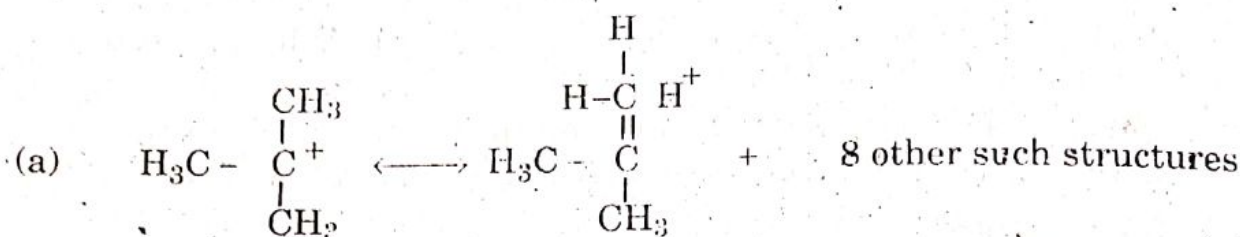
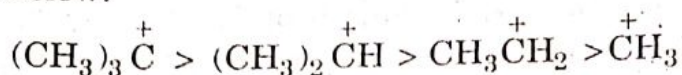
shown below.

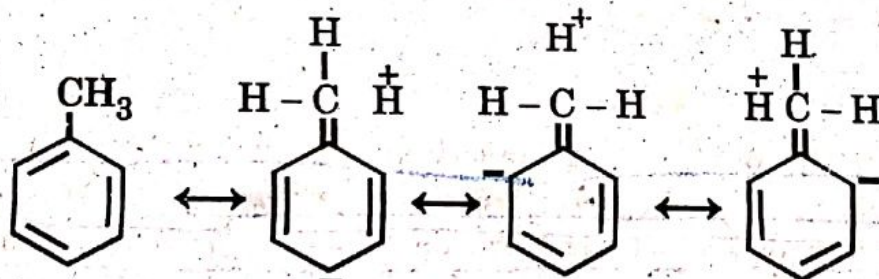
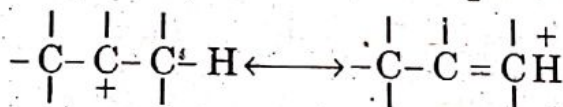
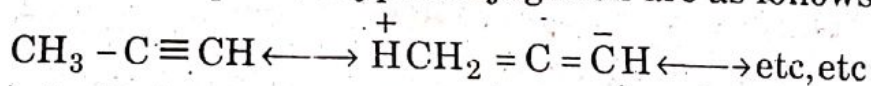
$$(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

(a) $H_3C-\overset{+}{C}(CH_3)-CH_3 \longleftrightarrow H_3C-C(CH_3)=CH_2\ H^+$ + 8 other such structures

(b) $CH_3-\overset{+}{C}H-CH_3 \longleftrightarrow H\overset{}{C}H_2=CH-CH_3\ (H^+)$ + 5 other such structures

(c) $CH_3-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{H}\ CH_2=CH_2$ + 2 other structures.

Other examples of hyperconjugation are as follows:

$$CH_3-C\equiv CH \longleftrightarrow \overset{+}{H}CH_2=C=\bar{C}H \longleftrightarrow \text{etc, etc}$$

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{+}{C}}-\overset{|}{\underset{|}{C}}-H \longleftrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{\underset{|}{C}}H\ \overset{+}{}$$

Toluene has a dipole moment due to hyperconjugation.

2.15 Hydrogen Bonding

"The electrostatic attraction between a hydrogen atom covalently bonded to a small, highly electronegative atom and a lone pair of electrons on highly electronegative atom in another molecule, is called **hydrogen bonding".** Hydrogen bond is represented by a dotted or dashed line. It is much weaker than a covalent or ionic bond but it is much stronger than the van der Waals attractive forces, i.e., the forces between the molecules of nonpolar compounds. It should be noted that:

(i) A hydrogen atom can participate in hydrogen bonding if it is bonded to O, N or F which have highly electronegativity and small atomic size.

(ii) Hydrogen bond is longer and much weaker than a normal covalent bond. The energies (strengths) of the hydrogen bonds are in the range 8 – 42 kJ/mol, while the O – H covalent bond dissociation energy in water is 464 kJ/mol.

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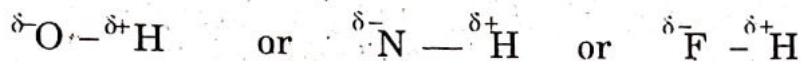
(iii) Hydrogen bonding results in long chains or clusters of a large number of associated molecules like many tiny magnets.

(iv) Like a covalent bond, hydrogen bond has a preferred bonding direction. This is attributed to the fact that hydrogen bonding occurs through *p* orbital which contain the lone pair of electrons on O, N or F atom.

Conditions for Formation of Hydrogen Bonding

(i) H atom is covalently bonded to O, N or F, i.e., the molecule must contain a polar bond.

$$^{\delta-}O - {}^{\delta+}H \quad \text{or} \quad {}^{\delta-}N - {}^{\delta+}H \quad \text{or} \quad {}^{\delta-}F - {}^{\delta+}H$$

(ii) The electronegative atom O, N or F in the polar bonds must have unshared electron pair.

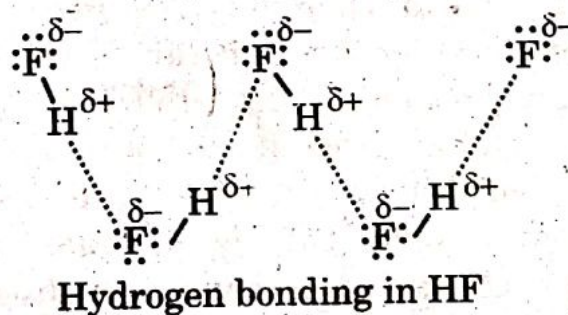
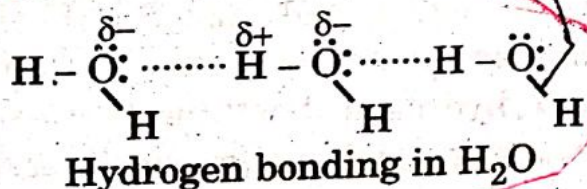
When hydrogen atom is covalently bonded to highly electronegative atom such as N, O or F, it carries partial positive charge and interacts with the lone pair of highly electronegative atom of another molecule near by. In general whenever polar molecules come near to one another, the positive end (δ^+) of one molecule interacts with the negative end (δ^-) of another because of electrostatic attraction between them and thus these molecules will associate together to form large clusters of molecules. In water and HF these interactions can be represented as:

example hydrogen

$$H - \overset{\delta-}{\ddot{O}}: \cdots\cdots \overset{\delta+}{H} - \overset{\delta-}{\ddot{O}}: \cdots\cdots H - \ddot{O}:$$
(each O also bonded to H)

Hydrogen bonding in H_2O

$$:\ddot{F}:^{\delta-} - H^{\delta+} \cdots :\ddot{F}:^{\delta-} - H^{\delta+} \cdots :\ddot{F}:^{\delta-} - H^{\delta+} \cdots :\ddot{F}:^{\delta-} - H^{\delta+} \cdots :\ddot{F}:^{\delta-}$$

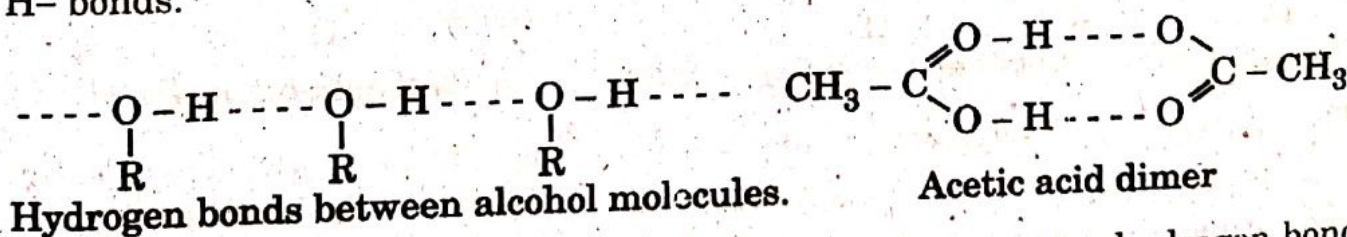
Hydrogen bonding in HF

Types of hydrogen bond. There are two types of hydrogen bonds.

(i) Intermolecular H – bonding (Association). This type of hydrogen bonding is between two or more similar or different molecules. As a result of this type of bonding two or more molecules are associated together. Ammonia, water, hydrogen fluoride, alcohols, carboxylic acids etc are the examples containing intermolecular H– bonds.

$$----\underset{R}{O}-H----\underset{R}{O}-H----\underset{R}{O}-H----$$

Hydrogen bonds between alcohol molecules.

$$CH_3 - C\begin{matrix} =O - H ---- O \\ -O - H ---- O \end{matrix}C - CH_3$$

Acetic acid dimer

Intramolecular H – bonding (Chelation). In some cases a hydrogen bonding can occur within a single molecule. This types of H – bonding is between two functional groups of the same molecule and thus leads to the formation of a ring structure. This

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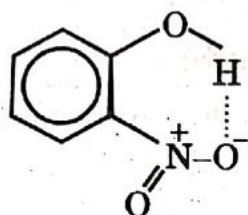
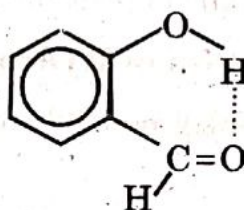
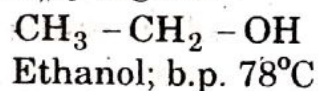
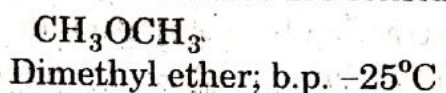
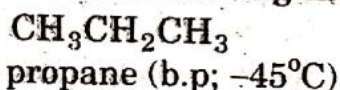
type of hydrogen bonding is therefore, a kind of chelation. *o*-hydroxybenzaldehyde (i.e., salicylaldehyde), *o-nitrophenol*, *o-chlorophenol* are the examples containing intramolecular hydrogen bonding.

o - nitrophenol Salicylaldehyde

Effects of Hydrogen bonding on various properties of organic compounds

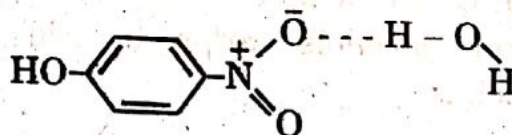
Hydrogen bonding has a significant effect on the physical properties (boiling points, solubility) of organic compounds. It is understandable that substances having nearly the same molecular masses have the same boiling point. The boiling points of alkanes and ethers of comparable molecular masses are not far apart, but the boiling points of alcohols having the same molecular masses are considerably higher.

$CH_3CH_2CH_3$ — propane (b.p; –45°C)

CH_3OCH_3 — Dimethyl ether; b.p. –25°C

CH_3-CH_2-OH — Ethanol; b.p. 78°C

This can be explained on the basis of hydrogen bonding. Ethanol forms hydrogen bonds and extra energy is required to break the hydrogen bonds holding the molecules together before it can be volatilized. Propane and dimethyl ether do not form hydrogen bonds and, therefore, have low boiling points.

If hydrogen bonding is possible between solute and solvent, this greatly increases solubtility of a substance. For example, substances like methanol and ethanol are highly soluble in water due to hydrogen bonding between their molecules. On the other hand, if hydrogen bonding is intramolecular and forms a chelate ring as in *o*-nitrophenol, then the hydrogen bonding between the solute and solvent is restricted and reduces solubility in H_2O. Thus solubility of *o*-nitrophenol in water is lower as compared to its *p*-isomer (*p*-nitrophenol) which is free to form hydrogen bonding with water.

Hydrogen bonding between alcohol and H_2O **p - nitrophenol in water**

The acidity of carboxylic acid is also effected by hydrogen bonding. *o*-hydroxybenzoic acid (salicylic acid) is approximately 40 times more acidic than *p*-hydroxybenzoic acid, because the anion produced after ionization of salicylic acid is stabilized through intramolecular hydrogen bonding, by chelation, whereas the anion of *p*-hydroxybenzoic acid has no intramolecular hydrogen bonding since the hydroxy group is far away from the carboxylate ion.

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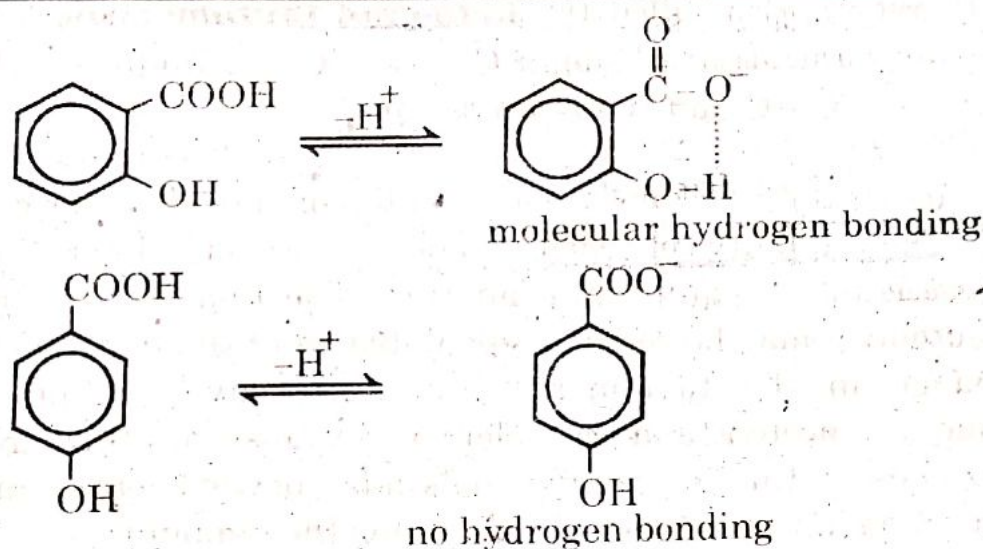
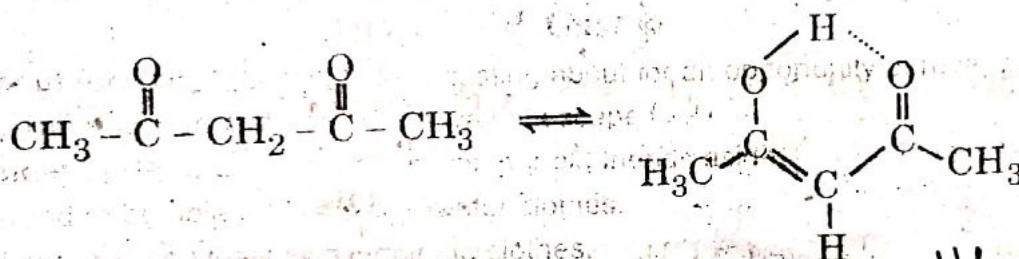
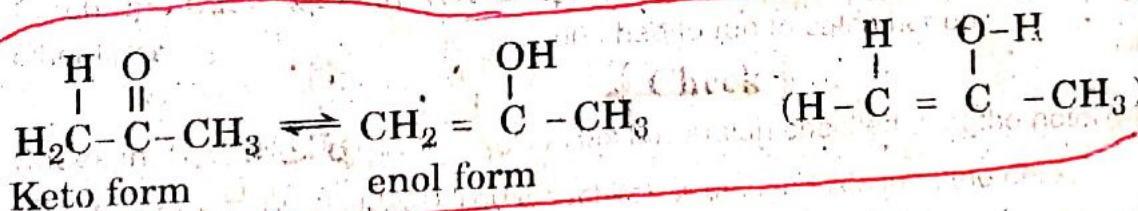
molecular hydrogen bonding

no hydrogen bonding

Intramolecular hydrogen bonding is also responsible for the large amount of enol present in certain tautomeric equilbria. The larger enol content (76.4%) in the equilibrium mixture of acetylacetone may be described to intramolecular hydrogen bonding.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons H_3C-C(-O-H\cdots O=)=CH-C-CH_3$$

2.16 Tautomerism

"Two structural isomers which differ in the relative positions of their atoms, exist in dynamic equilibrium, and are readily interconvertible, are called ***tautomers****, the phenomenon is called* ***tautomerism*** *and their interconversion is called* ***tautomerization****".* Tautomerism that involves transfer of a proton from one part of the molecule to another is called **proton tautomerism.** The most common examples of proton tautomerism are provided by the carbonyl compounds containing α-hydrogen, in which the proton from the α–carbon atom shifts to the carbonyl oxygen, and a pair of electron shifts from the C–H bond to C – C bond, to form an enol (from ene + ol,i.e., unsaturated alcohol). This process is called **enolization.** The proton then moves back to convert the enol form into the keto form.

$$\underset{\text{Keto form}}{H_2C(H)-\overset{O}{\overset{\|}{C}}-CH_3} \rightleftharpoons \underset{\text{enol form}}{CH_2=\overset{OH}{\overset{|}{C}}-CH_3} \quad (H-\overset{H}{\overset{|}{C}}=\overset{O-H}{\overset{|}{C}}-CH_3)$$

The tautomers containing the carbonyl group ($>C=O$) is designated as the keto form. The other one containing a hydroxyl group attached to a doubly bonded carbon is called **enol form.** Since, there is a rapid equilibrium between the keto and

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the enol forms, it is therefore, also called the **keto-enol tautomerism.** The keto form differs from the enol form in possessing a C – H, a C – C and a C = O bond where the enol has a C = C, a C – O and O – H bond.

Since the keto and the enol forms exist as interconvertible mixture, their isolation is difficult. The stability of each isomer, however, determines the percentage of each present in the equilibrium mixture. The relative stabilities (or energies) of the two tautomers may be roughly calculated from the bond energies of the bonds which change in the tautomerism. In this way we find that a monocarbonyl compound (i.e., acetone and acetaldehyde) is substantially more stable than its corresponding enol, and in fact simple enols have never been isolated and are known only as reaction intermediates. In acetone, the amount of enol form present at equilibrium is much less than 1% ; in acetaldehyde the enol content is too small to be detected. The keto form is more stable by about 69 kJ/mol. The greater stability of the keto forms of monocarbonyl compounds can be related to the greater strength of the carbon – oxygen π bond compared to the carbon – carbon bond.

Acetaldehyde: $CH_3-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons CH_2=\overset{OH}{\overset{|}{CH}}$

99.9 % 0.1 %

Acetone: $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_2=\overset{OH}{\overset{|}{C}}-CH_3$

(> 99%) (1.5 × 10^{-4})

In compounds whose molecules have two carbonyl groups separated by a methylene group ($-CH_2-$), (called β-dicarbonyl compounds), the amount of enol present at equilibrium is far higher. For example, 2,4-pentanedione exists in the enol form to an extent of 76%.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3$$ 2,4-pentanedione

Keto form (24%) enol form (76%)

The greater stability of the enol form of β-dicarbonyl compounds can be attributed to stability gained through hydrogen bonding in a cyclic form and to resonance.

H Hydrogen bond

:O: :O: ⟷ $^+$O: :O:$^-$

CH_3–C=C(H)–C–CH_3 ⟷ CH_3–C–C(H)=C–CH_3

Similarly, in acetoacetic ester, the enol is also stabilized by internal hydrogen bonding, which is unavailable to keto form.

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$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

92% Acetoacetic ester 8 %

H-bond: $H_3C-C(-O-H\cdots O=)C(-OC_2H_5)$ with $=C(H)-$ (intramolecular hydrogen-bonded enol)

Either the ketone or its tautomeric enol may lose a proton to form an intermediate **enolate ion** (described by two resonance structures), which may then recombine to give either tautomer.

$$R-\overset{:\ddot{O}}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}H_2 \rightleftharpoons \left[R-\overset{:\ddot{O}}{\overset{\|}{C}}-\bar{\ddot{C}}H_2 \leftrightarrow R-\overset{:\ddot{O}:^-}{\overset{|}{C}}=CH_2\right]+\overset{+}{H} \rightleftharpoons R-\overset{:\ddot{O}H}{\overset{|}{C}}=CH_2$$

Ketone Enol

Since tautomerization involves the transfer of a proton, it is catalysed by both acids and bases.

$$R-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}\langle + B: \rightleftharpoons \left[R-\overset{O}{\overset{\|}{C}}-\bar{\ddot{C}}\langle \leftrightarrow R-\overset{O^-}{\overset{|}{C}}=C\langle\right]+\overset{+}{B}H \rightleftharpoons R-\overset{OH}{\overset{|}{C}}=C\langle + B:$$

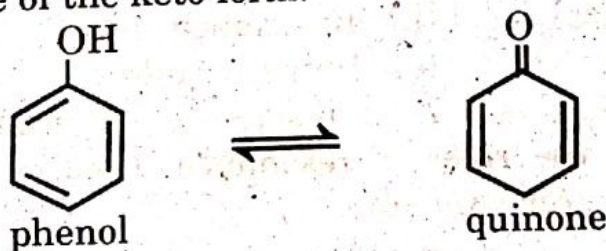
Ketone

The extent of enolization is greatly affected by solvent, concentration and temperature. For example, acetoacetic ester has an enol content of 0.4% in water and 19.8% in toluene. Water stabilizes the carbonyl group by making hydrogen bond with it, making this group less available for internal hydrogen bonding.

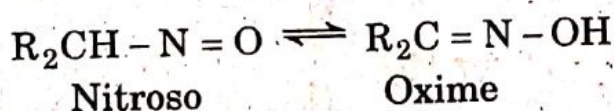
There are other types of tautomerism which also involve a rapid shift of proton, similar to the keto-enol tautomerism.

1. Phenol - keto tautomerism. For simple phenols equilibrium lies well on the side of phenol, since aromaticity is on the side of phenol. For phenol itself there is no evidence for the existence of the keto form.

phenol (OH on benzene ring) $\rightleftharpoons$ quinone (cyclohexadienone, C=O)

phenol quinone

2. Nitroso-oxime tautomerism. Oximes are more stable than the nitro compounds. As a rule nitro compounds are stable only when there is no α- hydrogen.

$$R_2CH-N=O \rightleftharpoons R_2C=N-OH$$

Nitroso Oxime

3. Nitro-aci-nitro tautomerism. Aliphatic nitro compounds are in equilibrium with aci forms. The nitro form is more stable than aci form.

$$R_2\overset{H}{\overset{|}{C}}-\overset{+}{N}(=O)O^- \rightleftharpoons R_2C=\overset{+}{N}(OH)O^-$$

Nitro form aci-nitro form

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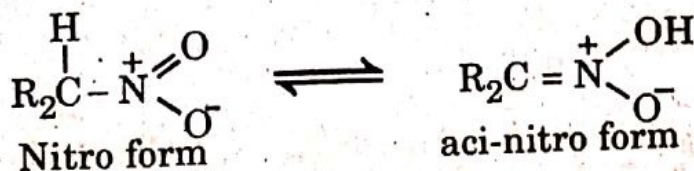
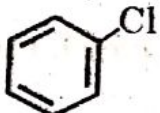
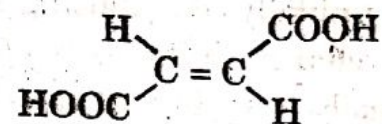
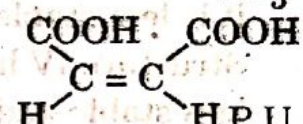
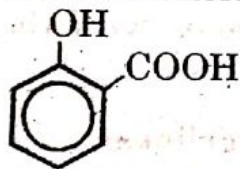
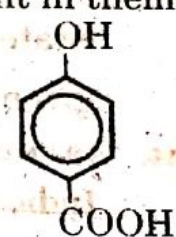
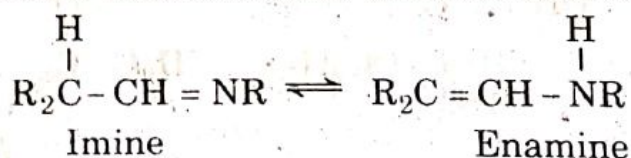

4. Imine-enamine tautomerism. Imine is more stable than enamine.

$$R_2\overset{H}{\overset{|}{C}}-CH=NR \rightleftharpoons R_2C=CH-\overset{H}{\overset{|}{N}}R$$

Imine Enamine

Questions

1. Explain the difference between:
(i) Atomic orbital and Molecular orbital.
(ii) Atomic orbital and a hybrid atomic orbital. (iii) Sigma and pi bond.
2. Discuss the following : (i) Heisenberg uncertainty principle.
(ii) Hund's rule. (iii) Pauli exclusion principle.
3. What are quantum numbers? State their significance. What is Aufbau principle?
4. Write detailed notes on any two of the following:
(a) Hybridization (b) delocalized Molecular orbitals.
(c) Conjugated system (d) Rules of Resonance P.U. 188,1994
5. Write detailed notes on any two of the following:
(a) Delocalized chemical bonding (b) Dipole moment
(c) Hyperconjugation (d) Resonance effect P.U. 1993
6. Write detailed notes on any two of the following:
(a) Hydrogen bonding (b)Tautomerism (c)Inductive effective P.U. 189,1992
7.(a) Explain the phenomenon of Resonance and its rules. P.U. 1998
(b) Draw the resonance contributing structures of the following compounds.
(i) Acetamide (ii) Aniline (iii) Pyridine
8. Define the following with examples:
(a) Molecular orbital (b) Resonance energy (c) Hyperconjugation
(d) Resonance effect (e) Inductive effect P.U. 1996
9. In each of the following sets of resonance structures, one structure is not valid according to the rules of resonance. Indicate which structure is not allowed and cite the relevant rule.

(a) $CH_3-\overset{+}{N}(=O)-O^- \longleftrightarrow CH_3-\overset{+}{N}(-O^-)=O \longleftrightarrow CH_3-N(=O)=O$

(b) $\underset{1}{CH_2=\overset{+}{N}=\bar{N}} \longleftrightarrow \underset{2}{\bar{C}H_2-\overset{+}{N}=N:} \longleftrightarrow \underset{3}{H_2C<(\ddot{N}=\ddot{N})}$ (3: ring)

(c) $\underset{1}{CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-\ddot{O}-C_2H_5} \leftrightarrow \underset{2}{CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O^-}{\overset{|}{C}}=O^+-C_2H_5} \leftrightarrow \underset{3}{CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{||}{C}}-O\,C_2H_5}$

(d) $\underset{1}{CH_3-\ddot{O}-CH=CH_2} \leftrightarrow \underset{2}{\bar{C}H_3=\overset{+}{O}-CH=CH_2} \leftrightarrow \underset{3}{CH_3-\overset{+}{O}=CH-\bar{C}H_2}$

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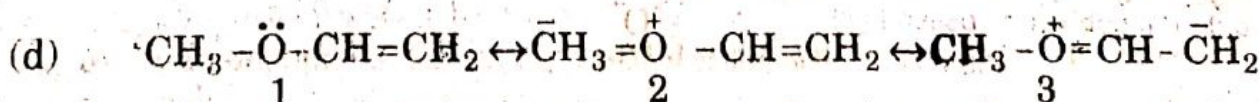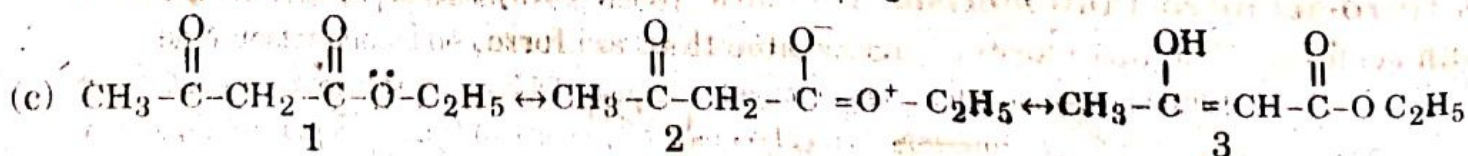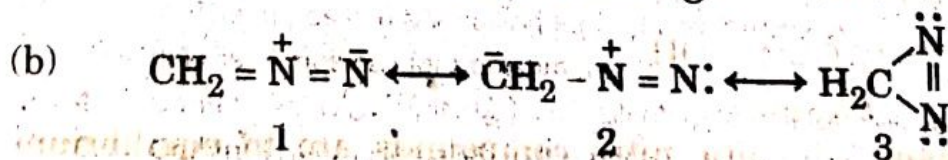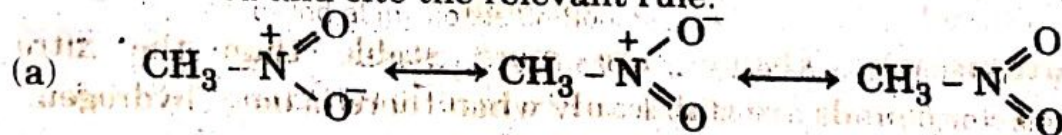
10. What are polar and nonpolar bonds? Give examples.
11. Explain and illustrate sp^3, sp^2 and sp hybridizations.
12. Explain why four covalent bonds in methane are equivalent.
13. Draw the molecular orbital picture of the following molecules and label each carbon the nature of hybridization and bond angles.
(i) $CH_2=C=CH_2$ (ii) CH_3CH_2OH (iii) CH_3NH_2 P.U. 1999
14. Which of the following compound show dipole moment?
(i) $CH_3-CH_2-CH_3$ (ii) $CH_3-C(=O)-CH_3$ (iii) $H-C(=O)-N(CH_3)_2$
(iv) C_6H_5Cl (v) $(H)(HOOC)C=C(COOH)(H)$ (vi) $(COOH)(H)C=C(COOH)(H)$ P.U.1999
15. **Discuss the rules to determine more important contributors to the resonance hybrid. Give examples.** P.U. 2002
16. **Draw the resonance structures of the following compounds.**
(i) $CH_2=CH-C(=O)-CH_3$ (ii) $CH_2=CH-C\equiv N$ (iii) $CH_3-C(=O)-CH_2-C(=O)-OC_2H_5$
(iv) $CH_3-\ddot{N}=\overset{+}{N}=\overset{-}{N}$
17. **Which of the following compound would participate in hydrogen bondings? Also indicate inter and intramolecular hydrogen bonding if present in them.**
(i) CH_4 (ii) o-HOC_6H_4COOH (iii) $CH_2=CH_2$ (iv) p-HOC_6H_4COOH
(v) CH_3OH (vi) Acetaldehyde (vii) Acetylacetone P.U. 1999

SHORT QUESTIONS

1. Arrange the s,p and the three sp-type hybrid atomic orbital in order of decreasing energy.

Ans. The more s character in the AO, the lower the energy. Therefore, the order of decreasing energy is: $p > sp^3 > sp^2 > sp > s$.

2. What effect does hybridization have on the stability of bonds?

Ans. Hybrid orbitals can (i) overlap better and (ii) provide greater bond angles, thereby minimizing the repulsion between pairs of electrons and making for greater stability.

3. Indicate which one of each of the following pairs of resonance structures is

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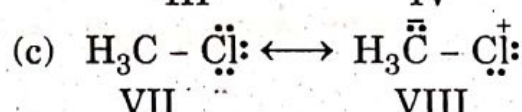
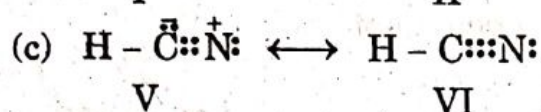
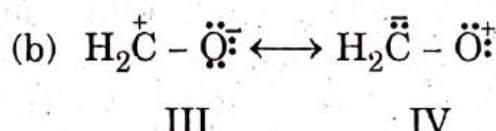
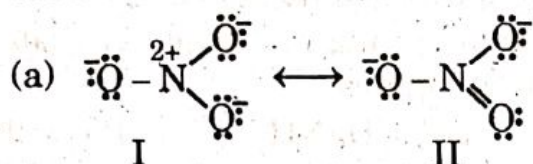
the less stable and is unlikely contributing structure. Give reason in each case.

(a) $:\ddot{O}-\overset{2+}{N}(\ddot{O}:)(\ddot{O}:) \longleftrightarrow :\ddot{O}-N(\ddot{O}:)(=\ddot{O}:)$ (b) $H_2\overset{+}{C}-\ddot{O}: \longleftrightarrow H_2\bar{C}-\ddot{O}:^+$

I II III IV

(c) $H-\bar{C}::\overset{+}{N}: \longleftrightarrow H-C:::N:$ (c) $H_3C-\ddot{Cl}: \longleftrightarrow H_3\bar{C}-\overset{+}{Cl}:$

V VI VII VIII

Ans. Structure I has fewer covalent bonds and has electron-deficient N, therefore, it is less stable and is an unlikely contributing structure.

(b) Structure IV has positive charge on the more electronegative O, therefore it is less stable and is an unlikely contributing structure.

(c) Structure V has fewer covalent bonds and a positive charge on more electronegative N, which is also electron deficient, therefore it is less stable and not valid.

(d) Carbon in structure VIII has 10 electrons; this is not possible with the elements of the second period.

4. Roughly, what kind of hybridization occurs if the interorbital bond angle is (a) 107°, (b) 118°, (c) 170°?

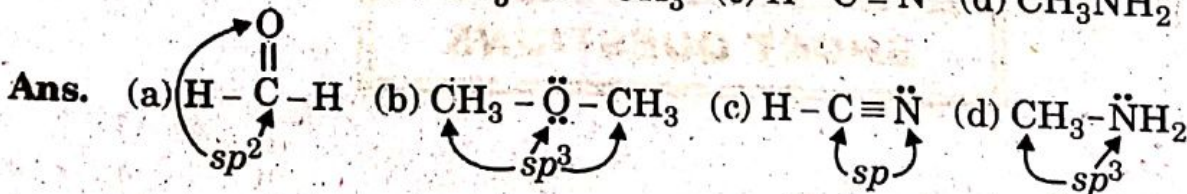
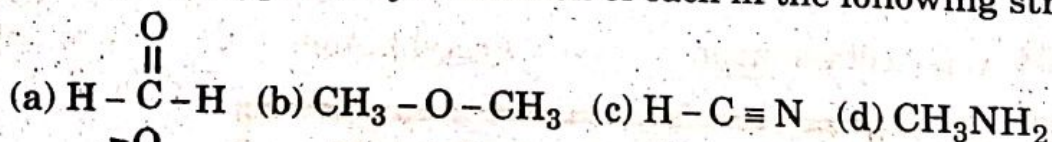
Ans. (a) sp^3, (b) sp^2, (c) sp.

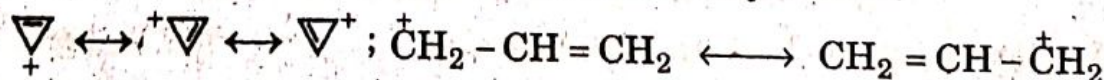
5. State the geometric shapes of molecules with the interorbital bond angles given (a) 107°, (b) 118°, (c) 165°

Ans. (a) tetrahedral (b) trigonal planar (c) linear.

6. Indicate the types of hybridization of each in the following structures:

(a) $H-\overset{O}{\overset{\|}{C}}-H$ (b) CH_3-O-CH_3 (c) $H-C\equiv N$ (d) CH_3NH_2

Ans. (a) $H-\overset{O}{\overset{\|}{C}}-H$ (sp^2) (b) $CH_3-\ddot{O}-CH_3$ (sp^3) (c) $H-C\equiv\ddot{N}$ (sp) (d) $CH_3-\ddot{N}H_2$ (sp^3)

7. Explain why $\overset{+}{\nabla}$ is more stable than $\overset{+}{C}H_2-CH=CH_2$?

The following three canonical forms can be written for cyclopropenyl cation, while for allyl cation two canonical forms can be written. Therefore cyclopropenyl cation is more stable than allyl cation.

$\overset{}{\underset{+}{\nabla}} \leftrightarrow {}^+\nabla \leftrightarrow \nabla^+$; $\overset{+}{C}H_2-CH=CH_2 \longleftrightarrow CH_2=CH-\overset{+}{C}H_2$

8. Why allyl cation, $\overset{+}{C}H_2-CH=CH_2$ is more stable than propyl cation, $CH_3-CH_2-\overset{+}{C}H_2$?

Ans. $\overset{+}{C}H_2-CH=CH_2$ is a conjugated unsaturated cation and two canonical forms

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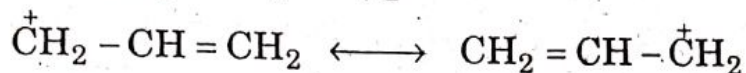
can be written for it, while for $CH_3 - CH_2 - \overset{+}{C}H_2$ no resonance structure can be written as it is nonconjugated cation. Therefore $\overset{+}{C}H_2 - CH = CH_2$ is more stable than $CH_3 - CH_2 - \overset{+}{C}H_2$.

$$\overset{+}{C}H_2 - CH = CH_2 \longleftrightarrow CH_2 = CH - \overset{+}{C}H_2$$

9. Why toluene has a dipole moment ?

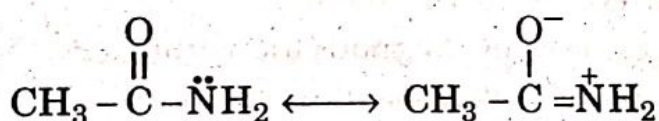
Ans. Toluene has a dipole moment due to hyperconjugation.
(See Hyperconjugation).

10. Why m-chlorobenzoic acid is a stronger acid than p-chlorobenzoic acid?

Ans. The Cl as substituent present at p-position is electron-withdrawing which is less due to resonance effect than at m-position because at m-position there is no resonance effect. Therefore, m-chlorobenzoic acid is a stronger acid than p-chlorobenzoic acid.

11. Why $CH_3 - \overset{O}{\overset{\|}{C}} - \ddot{N}H_2$ is much weaker base than $CH_3\ddot{N}H_2$?

Ans. The electron pair on N in acetamide is delocalized while the electron pair on $CH_3\ddot{N}H_2$ is localized, therefore acetamide is much weaker base than $CH_3\ddot{N}H_2$.

$$CH_3 - \overset{O}{\overset{\|}{C}} - \ddot{N}H_2 \longleftrightarrow CH_3 - \overset{O^-}{\overset{|}{C}} = \overset{+}{N}H_2$$

12. Why phenol is a stronger acid than ethanol?

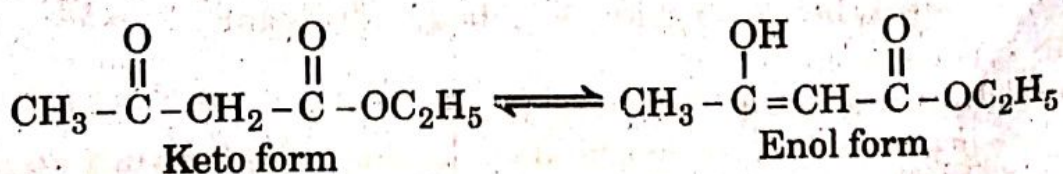
Ans. Phenolate ion is resonance stabilized (see resonance structures of phenoxide ion) while the negative charge on the alkoxide anoin, RO^- ,is not delocalized, therefore phenol is a stronger acid than ethanol.

13. Why ethanol has higher boiling point than dimethyl ether?

Ans. Ethanol forms hydrogen bonds and extra energy is required to break the hydrogen bonds holding the molecules together before it can be volatilized. Dimethyl ether do not from hydrogen bonds, therefore ethanol has higher boiling point than dimethyl ether.

14. Explain why acetoacetic ester gives ferric chloride test which is a typical test for phenol?

Ans. Acetoacetic ester is, in fact, a mixture of keto and enol forms which are always in equilibrium with each other.

$$\underset{\text{Keto form}}{CH_3 - \overset{O}{\overset{\|}{C}} - CH_2 - \overset{O}{\overset{\|}{C}} - OC_2H_5} \rightleftharpoons \underset{\text{Enol form}}{CH_3 - \overset{OH}{\overset{|}{C}} = CH - \overset{O}{\overset{\|}{C}} - OC_2H_5}$$

Therefore, it gives a ferric chloride test which is a characteristic test for

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enolic group ($>C=\overset{|}{C}-OH$).

15. Explain why?

(i) Chloroacetic acid is a stronger acid than acetic acid.

Ans. See in inductive effect.

(ii) Formic acid is a stronger acid than acetic acid.

Ans. See answer in inductive effect.

(iii) Tertiary carbocation is more stable than primary carbocation.

Ans. The more hyperconjugation structures that can be written for a species, the more stable is the species. Nine hypercojugation structures for tertiary carbocation and three for primary carbocation can be written (see structures in hyperconjugation). Therefore, tertiary carbocation is more stable than primary carbocation.

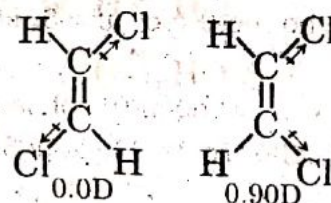
(iv) Methylamine is more basic than aniline.

Ans. See Answer in resonance effect.

(v) Acetylene has shorter bond length than ethylene.

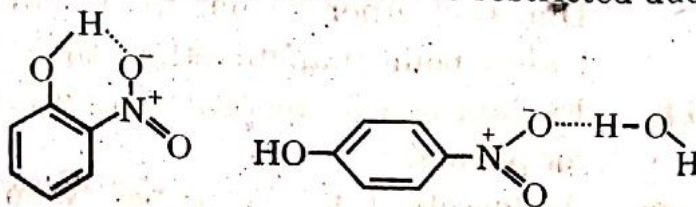
Ans. See answer in bond lengths.

(vi) *cis*-1,2-dichloroethylene has dipole moment but trans-1,2-dichloroethylene does not.

Ans. Trans-1,2-dichloroethylene does not exhibit any dipole moment because the individual bond moments are cancelled out due to the symmetry of the molecule while, cis isomer has a dipole due to individual bond moments.

(vii) The C-Cl bond length is shorter in vinyl chloride than in CH_3CH_2Cl.

Ans. The C-Cl bond is polarized both in vinyl chloride and ethyl chloride. However, the vinyl chloride is a hybrid of resonance structures such as $CH_2=CH-\ddot{C}l \leftrightarrow \bar{C}H_2-CH=\overset{+}{C}l$. The resonance effect is absent in CH_3CH_2Cl. Therefore, the C-Cl bond length is shorter in vinyl chloride than in CH_3CH_2Cl.

16. Why the solubility of *o*-nitrophenol is lower than the *p*-nitrophenol?

Ans. In *o*-nitrophenol, the hydrogen bonding with water molecule is restricted due to its intramolecular hydrogen bonding while *p*-nitrophenol is free to form hydrogen bonding with water, therefore the solubility of *o*-nftrophenol is lower than *p*-nitrophenol.

17. Why *o*-Hydroxybenzoic acid is about 40 times more acidic than *p*-hydroxybenzoic acid?

Ans. See in hydrogen bonding.

18. Why does acetoacetic ester reacts like a ketone as well as like an alkene?

Ans. Acetoacetic ester shows tautomerisim, in which the keto form is in dynamic

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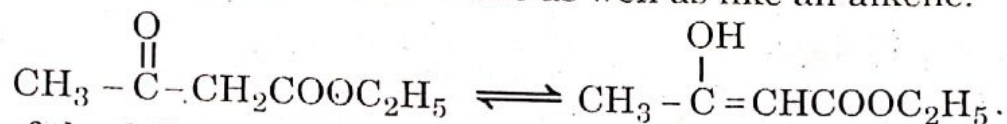
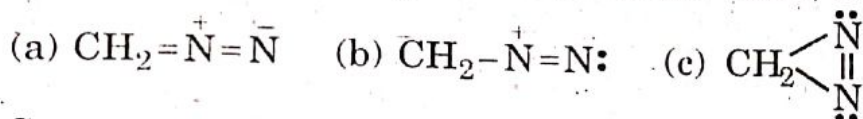
equilibrium with the enol form which provides an alkene group, therefore, acetoacetic ester reacts like a ketone as well as like an alkene.

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CHCOOC_2H_5$$

19. Which of the following structures is not valid, cite the relavent rule:

(a) $CH_2=\overset{+}{N}=\overset{-}{N}$ (b) $CH_2-\overset{+}{N}=N:$ (c) CH_2 ring with $\ddot{N}=\ddot{N}$

Ans. Structure (c) is not valid because it shows the movement of N atoms.

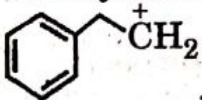
20. Which one of the following is a stronger acid and why? $CH_3CH_2CH_2COOH$ and $(CH_3)_2CHCOOH$.

Ans. The electron donating inductive effect of alkyl group is more at α-carbon than at β-carbon. Therefore, $(CH_3)_2CHCOOH$ is a weaker acid than $CH_3CH_2CH_2COOH$.

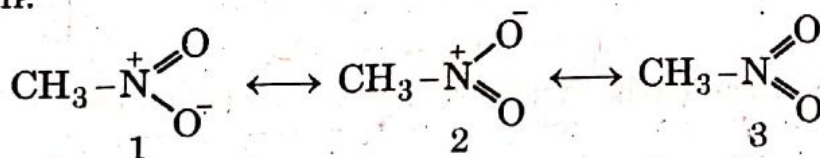
21. Why the C–Cl bond length is shorter in $CH_2=CH-Cl$ than CH_3-CH_2-Cl?

Ans. The resonance structures of vinyl chloride, $CH_2=CH-Cl \leftrightarrow {}^{-}CH_2-CH=Cl^{+}$ show that the C–Cl bond length lies between single and double bond, therefore, C–Cl bond length is shorter than C–Cl single bond length of CH_3CH_2-Cl, because in CH_3CH_2Cl there is no resonance.

22. Why the carbocation $CH_2=CH-\overset{+}{C}H_2$ is more stable than $CH_3-CH_2-\overset{+}{C}H_2$?

Ans. In $CH_2=CH-\overset{+}{C}H_2$ the charge on carbon is stabilized more due to resonance $CH_2=CH-\overset{+}{C}H_2 \leftrightarrow \overset{+}{C}H_2-CH=CH_2$ while in $CH_3CH_2\overset{+}{C}H_2$ there is no resonance.

23. Which of the following contributing structures of nitromethane is not valid? Explain.

$$CH_3-\overset{+}{N}{\overset{\nearrow O}{\searrow O^-}} \longleftrightarrow CH_3-\overset{+}{N}{\overset{\nearrow O^-}{\searrow O}} \longleftrightarrow CH_3-N{\overset{\nearrow O}{\searrow O}}$$

1   2   3

Ans. Structure 3 is not valid because nitrogen has five covalent bonds. According to rules of resonance N can have 4 covalent bonds at the maximum.

Multiple Choice Questions

1. The orbitals providing the most efficient overlap are:

(a) s–s (b) sp–sp (c) sp^2-sp^2 (d) sp^3-sp^3 **Ans:(b)**

2. The compound $CH_3CH=CH_2$ has a bond formed by the overlap of which of the following hybrid orbitals?

(a) sp^2-sp^3 (b) sp^3-sp^3 (c) $sp-sp^2$ (d) $sp-sp^3$ **Ans:(a)**

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3. Which of the following free radicals is the most stable?
(a) $CH_3^{\bullet}$ (b) $(CH_3)_2CH^{\bullet}$ (c) $(CH_3)_3C^{\bullet}$ (d) $(CH_3)_2CHCH_2^{\bullet}$ **Ans:(c)**

4. Which of the following carbocation is the most stable?
(a) $(CH_3)_2\overset{+}{C}H$ (b) $\overset{+}{C}H_3$ (c) $CH_3\overset{+}{C}H_2$ (d) $(CH_3)_3\overset{+}{C}$ **Ans:(d)**

5. Which of the following has a bond formed by the overlap of an sp^2 hybrid orbital with an sp hybrid orbital?
(a) $CH_2=CH_2$ (b) $CH_2=C=CH_2$
(c) $CH_3C\equiv CCH_2CH_3$ (d) $CH_2=CHCH_3$ **Ans:(b)**

6. Which of the following is most basic?
(a) CH_3OH (b) H_2O (c) CH_3NH_2 (d) NH_3 **Ans:(c)**

7. Which of the following compounds participate in hydrogen bonding?
(a) CH_3Cl (b) CH_3OCH_3 (c) CH_3CH_2Cl (d) CH_3NH_2 **Ans:(d)**

8. Which of the following is valid as resonance structure of the pentadienyl cation?
(a) $CH_2=CH-CH=CH-\overset{+}{C}H_2$ (b) $CH_3-CH=CH-CH=\overset{+}{C}H_2$
(c) $CH_2=CH-CH=\overset{+}{C}-CH_3$ (d) All of the above **Ans:(a)**

9. Which of the following is the least basic?
(a) NH_3 (b) $(CH_3)_3N$ (c) $C_6H_5NH_2$ (d) CH_3NH_2 **Ans:(c)**

10. Which of the following acids is the strongest acid?
(a) CH_3COOH (b) $ClCH_2COOH$ (c) F_3CCOOH (d) Cl_3CCOOH **Ans:(c)**

11. Which of the following is not a conjugated unsaturated system.
(a) allyl radical (b) allyl cation
(c) 1,3-butadiene (d) 1-penten-4-yne **Ans:(d)**

12. The hybridization of the carbocation in the reaction intermediate shown is
$C_6H_5-\overset{+}{C}H_2$
(a) *sp* (b) sp^2 (c) sp^3 (d) sp^3d **Ans: (b)**

13. Which of the following compounds will show hydrogen bonding?
(a) $CH_3-CH_2CH_3$ (b) CH_3COCH_3 (c) $CH_3C\equiv N$ (d) CH_3NH_2 **Ans: (d)**

14. The equilibrium of two readily interconvertible isomers is called
(a) stereoisomerism (b) metamerism
(c) tautomerisim (d) polymorphism **Ans: (c)**

15. Which of the following contributing structures of acraldehyde is not important?
(a) $CH_2=CH-CH=\ddot{O}:$ (b) $CH_2=CH-\overset{+}{C}H-\ddot{O}:^-$
(c) $CH_2=CH-\overset{-}{C}H-\overset{+}{O}:$ (d) $\overset{+}{C}H_2-CH=CH-\ddot{O}:^-$ **Ans: (c)**

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16. Which of following compounds does not show hydrogen bonding?
(a) CH_3OH (b) CH_3OCH_3 (c) NH_3 (d) HF **Ans: (b)**

17. Which of the following compounds has a delocalized bonding?
(a) $CH_2 = CH - CH = CH_2$ (b) $CH_3 - CH = CH - CH_3$
(c) $CH_3 - CH_2 - CH_2 - CH_3$ (d) $CH_2 = CH - CH_2 - CH = CH_2$ **Ans: (a)**

18. Which one of the following is not electron-withdrawing inductive effect.
(a) COR (b) Cl (c) CH_2R (d) OH **Ans: (c)**

19. The polarization of a bond induced by an adjacent polar bond through σ bond is called:
(a) resonance effect (b) inductive effect
(c) hyperconjugation (d) steric effect **Ans: (b)**

20. Which one of the following is not conjugated molecule.
(a) cyclohexene (b) acetamide (c) phenol (d) benzene **Ans: (a)**

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3. NOMENCLATURE OF ORGANIC COMPOUNDS

There are two general ways of naming organic compounds;

(i) Common or trivial and (ii) Systematic names (IUPAC names).

3.1. Trivial Or Common names

During the first half of the nineteenth century, chemists discovered many new compounds and named them with little or no structural significance. Such *common* or *trivial* names might reflect the source of the compound, the method of its preparation or the name of the person working on it. For example, acetic acid can be obtained from vinegar, it got its name from the Latin word for vinegar, acetum. Formic acid, HCOOH, was so named as it was obtained by distillation of red ants (Latin, *formica* = ants). Ethylene chloride got its name because it was made by the reaction of ethylene with chlorine. Barbituric acid is said to perpeturate the name of woman barbara. Some names, refer to distinctive properties that characterize the compound, e.g; acrolein (Latin acris; pungent); chrysene (Greek chrysos, golden); glucose (Greek glucose, sweet) refer to attributes of odour, colour and taste.

An ordinary name given to a compound without reference to its structure is called a **Common name** or **Trivial name**. *The common names are like nicknames.*

Common or trivial names are still widely used by chemists, biochemists and the companies that sell chemicals. For this reason, trivial names have a firm place in the literature and language of organic chemistry and hence it is still necessary to learn the common names for some of the common compounds.

3.2. Systematic Naming of Organic Compounds by IUPAC System

With the rapid growth of organic chemistry, the number of compounds increased fantastically (now about 3 million). It becomes impossible to give common names to such a large number of organic compounds.

In 1957, the International union of Pure and Applied chemistry evolved a scheme for giving systematic names to organic compounds on the basis of structure. This is known as the **IUPAC System**. The systematic name of a compound derived from its structural formula by applying IUPAC rules, is referred to its as **IUPAC Name**. One organic compounds can have only one IUPAC name. It is superior to a common name as it gives an insight into the structure of the molecule. Knowing the IUPAC name of a compounds, we can at once write its structural formula. *Remember that the common names identify compounds while the IUPAC names represent structures.*

The IUPAC system of nomenclature is based upon the following principles for assignment of substitutive names.

1. The longest continuous carbon chain (the parent chain) containing the functional group is the parent structure of aliphatic (acyclic) compounds.
2. The common names of familiar cyclics are frequently chosen as parent structures of compounds containing cyclic structures.
3. An order of preference is assigned to various functional groups. The groups higher in the order are given preference in the definition of parent structures. Some functional groups are always considered as substituents.

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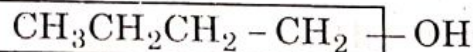
Functional Group

A functional group is an atom or group of atoms in a molecule that gives the molecule its characteristic chemical properties. Double and triple bonds are functional groups. Other examples include -Cl, –Br, –OH, $–NH_2$, –COOH, $>C=O$ groups.

$$\boxed{CH_3CH_2CH_2-CH_2} \;|\; OH$$

Hydrocarbon portion Functional group

The concept of functional group is important to organic chemistry for three reasons:

1. *Functional groups serve as basis for nomenclature.*
2. *Functional groups serve to classify organic compounds into classes / families. All compounds with the same functional group belong to the same class.*
3. *Functional group is a site of chemical reactivity in a molecule. Compounds in the same class have similar chemical properties.*

Alkyl groups

Radicals which are derived by the removal of one hydrogen atom from an alkane are called **alkyl radicals** and are expressed by general formula, C_nH_{2n+1}. The names of the alkyl groups are derived by replacing the ending -ane of the corresponding alkane by -yl. An alkyl group is represented by a general symbol R-. Two different alkyl groups (n-propyl and isopropyl) are derived from propane depending on whether the hydrogen atom is removed from the terminal or the middle carbon of propane. Similarly, two alkyl groups are obtained from each of n-butane and isobutane. Some of the common alkyl groups are given below:

Methyl	CH_3-	Ethyl	CH_3CH_2-
n-propyl	$CH_3CH_2CH_2-$	Isopropyl	$CH_3-\underset{\vert}{CH}-CH_3$
n-butyl	$CH_3CH_2CH_2CH_2-$	Sec butyl	$CH_3-CH_2-\overset{\vert}{CH}-CH_3$
Isobutyl	$CH_3-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-$	tert-butyl	$CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-$
n-pentyl	$CH_3CH_2CH_2CH_2CH_2-$	Isopentyl	$CH_3-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-CH_2-$
tert.pentyl	$CH_3CH_2-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-$	Neopentyl	$CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH_2-$

An alkyl group is known as primary if its carbon of attachment is bonded to only one other carbon atom, secondary if bonded to two other carbon atoms, and tertiary if

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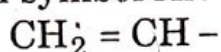
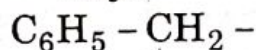
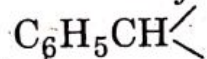
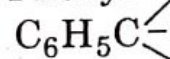
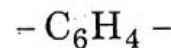
bonded to three other carbon atoms. Thus isopropyl group is a secondary alkyl group but isobutyl group is a primary alkyl group.

Unsaturated hydrocarbon groups are called *alkenyl groups*, while the aromatic hydrocarbon groups are called *aryl groups* and are represented by the general symbol Ar.

$CH_2=CH-$ Vinyl	$CH_2=CH-CH_2-$ Allyl	C_6H_5- Phenyl	$-C_6H_4-$ Phenylene
$C_6H_5-CH_2-$ Benzyl	$C_6H_5CH<$ Benzal	$C_6H_5C\equiv$ Benzo	

1. Alkanes

*Hydrocarbons that contain only single bonds are called **alkanes**.* Hydrocarbons are compounds that contain only carbon and hydrogen. The first four members of the series are known by their common names; methane, ethane, propane and butane. The names of higher alkanes are derived from the Greek prefixes that indicate the number of carbon atoms in the molecule. Thus *pentane* has 5 carbons, *hexane* has 6 and so on.

Table 3.1. Names of the unbranched alkanes

Name	No. of Carbons	Structure	Name	No. of Carbons	Structure
Methane	1	CH_4	Eicosane	20	$CH_3(CH_2)_{18}CH_3$
Ethane	2	CH_3CH_3	Heneicosane	21	$CH_3(CH_2)_{19}CH_3$
Propane	3	$CH_3CH_2CH_3$	Docosane	22	$CH_3(CH_2)_{20}CH_3$
Butane	4	$CH_3(CH_2)_2CH_3$	Triacontane	30	$CH_3(CH_2)_{28}CH_3$
Pentane	5	$CH_3(CH_2)_3CH_3$	Hentriacontane	31	$CH_3(CH_2)_{29}CH_3$
Hexane	6	$CH_3(CH_2)_4CH_3$	Tetracontane	40	$CH_3(CH_2)_{38}CH_3$
Heptane	7	$CH_3(CH_2)_5CH_3$	Pentacontane	50	$CH_3(CH_2)_{48}CH_3$
Octane	8	$CH_3(CH_2)_6CH_3$	Hexacontane	60	$CH_3(CH_2)_{58}CH_3$
Nonane	9	$CH_3(CH_2)_7CH_3$	Heptacontane	70	$CH_3(CH_2)_{68}CH_3$
Decane	10	$CH_3(CH_2)_8CH_3$	Octacontane	80	$CH_3(CH_2)_{78}CH_3$
Undecane	11	$CH_3(CH_2)_9CH_3$	Nonacontane	90	$CH_3(CH_2)_{88}CH_3$
Dodecane	12	$CH_3(CH_2)_{10}CH_3$	Hectane	100	$CH_3(CH_2)_{98}CH_3$
Tridecane	13	$CH_3(CH_2)_{11}CH_3$			

In the **common** system all isomeric alkanes have the same parent name. The name of various isomers are distinguished by prefixes. The prefix indicates the type of branching present in the molecule.

The prefix n-(normal) denotes an unbranched chain of C atoms. The prefix iso-indicates a CH_3 branch on the second carbon from the end. The prefix neo–indicates two methyl groups attached to the second carbon from the end of the continuous chain.

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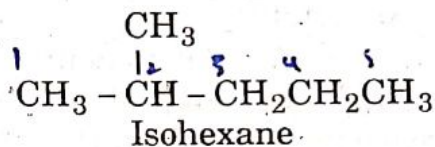
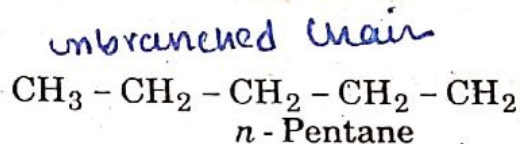
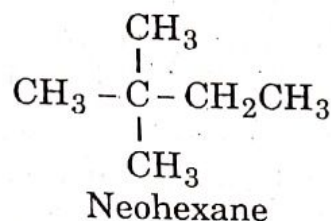
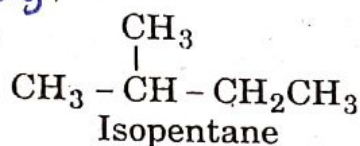
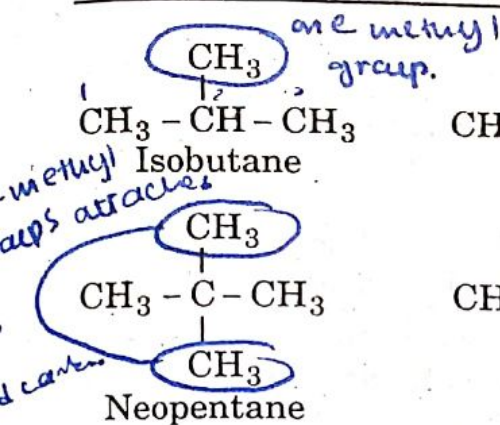
$$CH_3-CH(CH_3)-CH_3$$
Isobutane

$$CH_3-CH(CH_3)-CH_2CH_3$$
Isopentane

$$CH_3-CH_2-CH_2-CH_2-CH_2$$
n-Pentane

$$CH_3-C(CH_3)_2-CH_3$$
Neopentane

$$CH_3-C(CH_3)_2-CH_2CH_3$$
Neohexane

$$CH_3-CH(CH_3)-CH_2CH_2CH_3$$
Isohexane

IUPAC Rules for Naming Alkanes

The IUPAC system is much the same for all classes of organic compounds. Branched-chain alkanes are named according to the following rules:

1. Find the longest continuous carbon chain in the molecule and name the alkane corresponding to this number of carbon atoms.
2. Number the carbon atoms of the longest chain starting from that end so as to assign the lowest possible total number to the substituents. If there are more than one longest chain, select the chain with greatest number of substituents.
3. The position of each substituent is specified by the number of carbon to which it is attached in the longest continuous chain.
4. When two or more substituents are present on the same carbon, use the number twice.
5. When two or more substituents are identical, indicate this by the use of prefixes di–, tri–, tetra–, and so on.
6. The substituents are written in alphabetical order before the parent name. Each substituent is prefixed by the number assigned to it and separated from the name by a hyphen. If several identical radicals are present, their numbers are listed together, separated each number by commas. Some examples are given below to illustrate the system.

$${}^{1}CH_3-{}^{2}C(CH_3)_2-{}^{3}CH_2-{}^{4}CH_2{}^{5}CH_3$$
2,2-dimethylpentane

$${}^{1}CH_3-{}^{2}CH_2-{}^{3}C(CH_3)(CH_2CH_3)-{}^{4}CH_2{}^{5}CH_2{}^{6}CH_3$$
3-ethyl 3-methylhexane

$${}^{8}CH_3-{}^{7}CH_2-{}^{6}CH_2-{}^{5}C(CH_3)(CH_2CH_3)-C(CH_2CH_3)(CH_2CH_3)-{}^{3}CH(CH_3)-{}^{2}CH_2-CH_3$$
4,4,5-Triethyl-3,5-dimethyloctane

$${}^{7}CH_3-{}^{6}CH_2-{}^{5}CH(CH_3)-{}^{4}CH(CH_2CH_2CH_3)-{}^{3}CH(CH_3)-{}^{2}CH(CH_3)-{}^{1}CH_3$$
2,3,5-trimethyl-4-propylheptane

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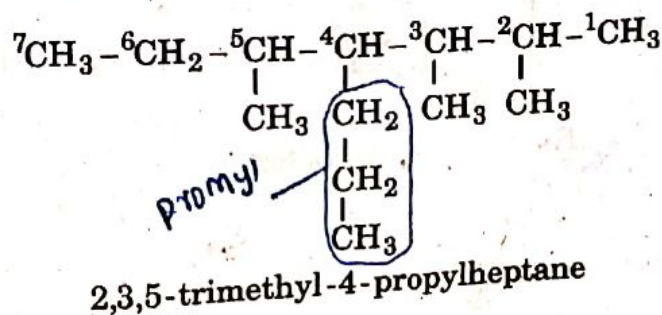
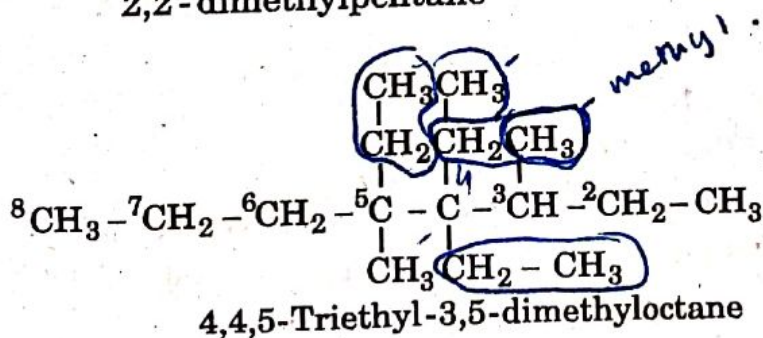
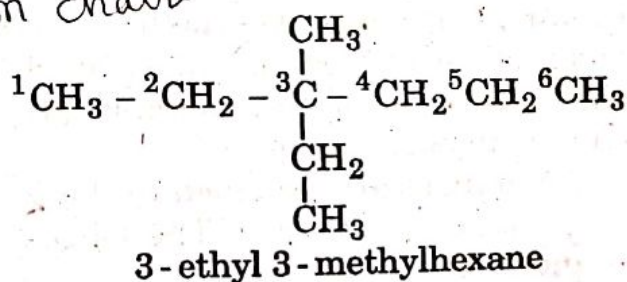
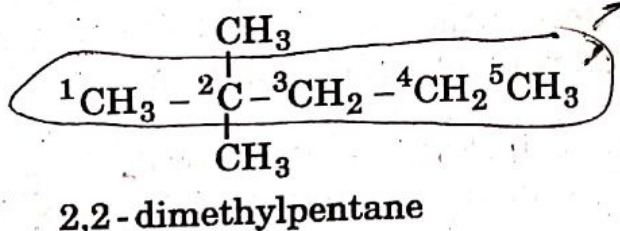
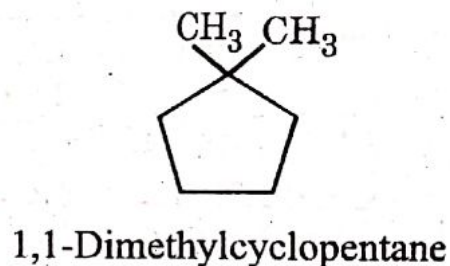
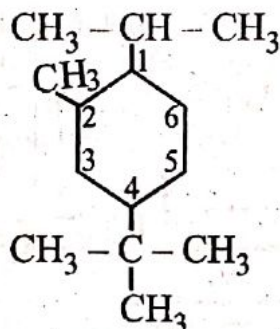
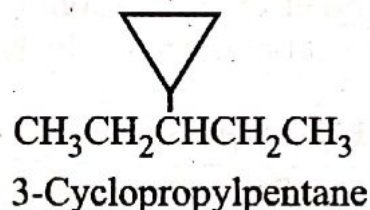
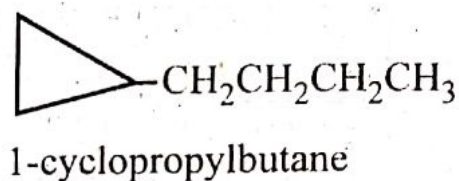
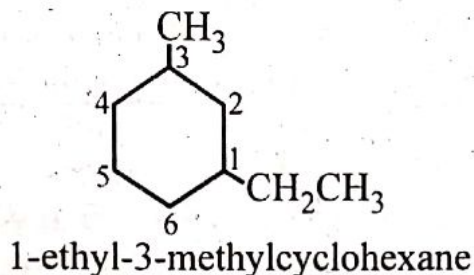
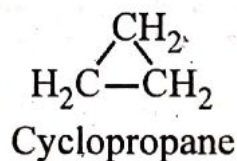

2. Cycloalkanes

Cycloalkanes with only one ring are named by adding the prefix cyclo- to the name of the alkane having the same number of carbons as in the ring. Cycloalkanes are often represented by simple geometrical figures. It should be noted that each corner represents CH_2 group.

Substituted cycloalkanes are named as alkyl cycloalkanes. The substituents on the ring are named, and their positions are indicated by numbers. The ring is numbered so that the substituents are given the lowest possible numbers.

The ring is designated as a substituent if the alkane chain contains a greater number of carbon atoms than the ring.

2 Rings. 4-tert-butyl-1-isopropyl-2- methylcyclohexane

Bicyclic Compounds Polycyclic compounds, in which two or more carbon atoms are common to two or more rings, take the name of an open chain compound having the same number of carbon atoms, and suffixes such as bicyclo- and tricylo indicate the number of rings. The points of fusion of the rings are indicated by listing the number of carbon atoms in each of the bridges. The bridges are listed, within brackets, in order of decreasing length. The numbers in brackets indicate how many atoms are in each bridge.

Numbers are assigned to the carbon atoms by beginning at a bridgehead and moving along the bridges. The longest bridge is numbered first, the second largest next and so on.

Bicyclo [2,2,1] heptane

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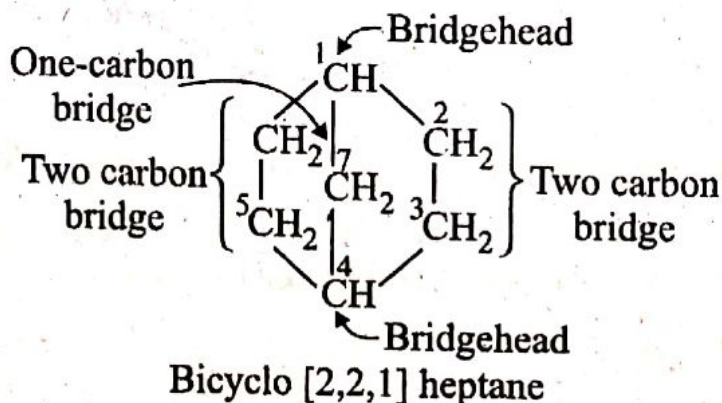
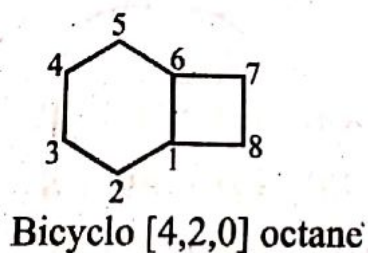
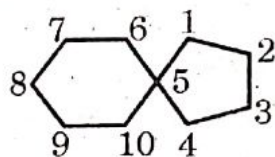
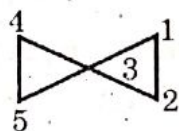
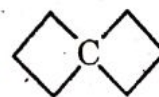
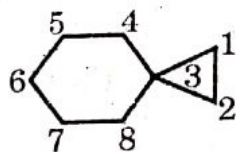
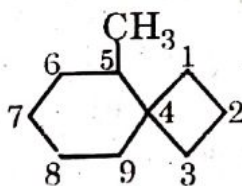

Spiroalkanes: A "spiro union" is one formed by a single atom which is the only common member of two rings. A "free Spiro union" is one constituting the only union direct or indirect between two rings. The common atom is designated as the "spiro atom". According to the number of spiro atoms present, the compounds are distinguished as monospiro–, dispiro–, trispirocompounds, etc. The following rules apply to the naming of spiroalkanes containing free spiro unions.

Monospiro compounds consisting of only two alicyclic rings as components are named by placing "spiro" before the name of the normal acyclic hydrocarbon of the same total number of carbon atoms. The number of carbon atoms linked to the spiro atom in each ring is indicated in ascending order in brackets placed between the spiro prefix and the alkane (hydrocarbon) name. The carbon atoms in monospiro alkanes are numbered consecutively starting with a ring atom next to the spiro atom, first through the smaller ring (if such be present) and then through the spiro atom and around the second ring.

Spiro [4.5] decane

Spiro [2.2] pentane

Spiro [3.3] heptane

Spiro [2.5] octane

5-methylspiro [3.5] nonane

1-methylspiro [3.5] nonane

Polyspiro compounds consisting of a linear assembly of three or more alicyclic systems are named by placing "dispiro–", "trispiro–" "tetraspiro–" etc., before the name of the unbranched–chain acyclic hydrocarbon of the same total number of carbon atoms. The numbers of carbon atoms linked to the spiro atoms in each ring are indicated in brackets in the same order as the numbering proceeds about the ring. Numbering starts with a ring atom next to a terminal spiro atom and proceeds in such a way as to give the spiro atoms as low numbers as possible after numbering all the carbon atoms of the first ring linked to the terminal spiro atom.

Dispiro [5.1.7.2] heptadecane

3. Alkenes

(i) Trivial or Common System. In this system of nomenclature alkenes are named by replacing the ending –ane of the corresponding alkane by -ylene, e.g., ethylene from ethane, propylene from propane and isobutylene from isobutane

$CH_2 = CH_2$
Ethylene

$CH_3 - CH = CH_2$
Propylene

$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$
Isobutylene

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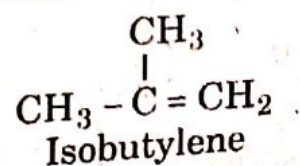
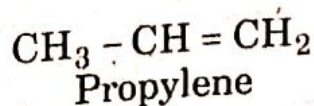
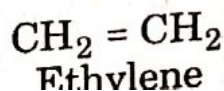
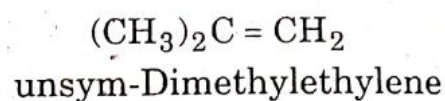
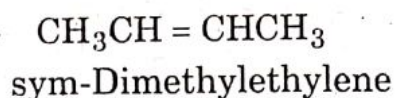
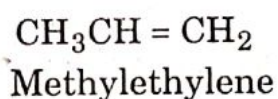
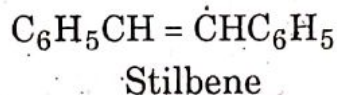
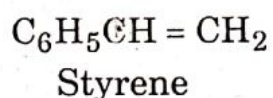

The use of trivial names becomes difficult for individual alkenes having four or more carbon atoms because of the large number of isomers possible. So the common names are used only for the above three alkenes. However, a few simple alkenes may be named as derivatives of ethylene, e.g.,

$CH_3CH = CH_2$	$CH_3CH = CHCH_3$	$(CH_3)_2C = CH_2$
Methylethylene	sym-Dimethylethylene	unsym-Dimethylethylene

A few special trivial names are also in common use, e.g.,

$C_6H_5CH = CH_2$	$C_6H_5CH = CHC_6H_5$
Styrene	Stilbene

(ii) IUPAC System. 1. Select the longest continuous chain containing the carbon - carbon double bond as the parent chain which is then named by replacing the ending –ane of the corresponding alkane by –ene.

2. The parent chain is numbered starting from the end nearer to the double bond.
3. The position of the double bond is indicated by putting the number of lower numbered carbon of the double bond before the name of the alkene.
4. Presence of more than one double bond is indicated by the suffix -diene for two double bonds, -triene for three double bonds and so on.
5. Indicate the locations of the substituent groups by the number of the carbon atoms to which they are attached.
6. For cycloalkenes, numbering is always started from one of the carbon atoms of the double bond such that when continued toward the other carbon of the double bond, the substituents (if any) are given the lowest sum of numbers. It is not necessary to specify the position of the double bond (unless there are more than one double bond in the ring) because it is always 1.

When a geometric isomer is to be specified, a prefix cis or trans is added.

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_3$$

2-Methyl-2-butene

$$CH_3CH_2-{}^5\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle {}^8CH_3\,{}^7CH_2\,{}^6CH_2}{\underset{|}{C}}}}-{}^4CH_2-{}^3CH_2-{}^2\overset{\displaystyle CH_3}{\overset{|}{C}}={}^1CH_2$$

5-Ethyl-2,5-dimethyl-1-octene

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle CH_2CH_2CH_3}{\overset{|}{CH}}-CH=CH_2$$

4,5-Dimethyl-3-propyl-1-hexene

$${}^1CH_2={}^2\underset{\displaystyle CH_3}{\underset{|}{C}}-{}^3CH={}^4CH_2$$

2-methyl-1,3-butadiene

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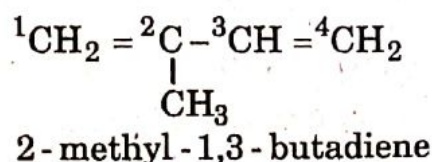
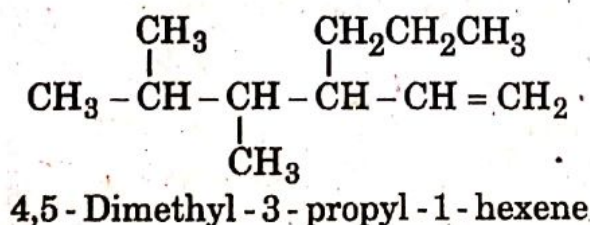
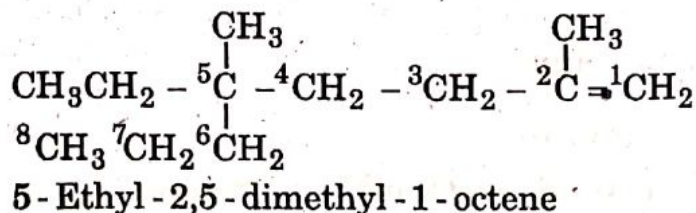
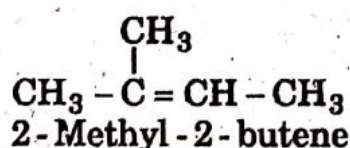
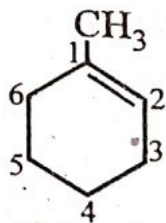
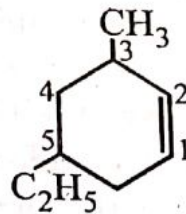
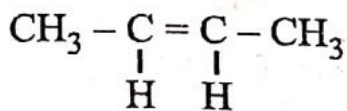
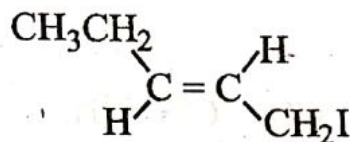
CH_3 (C1), ring positions 1–6

1-Methylcyclohexene

CH_3 (C3), C_2H_5 (C5), ring positions 1–5

5-Ethyl-3-methylcyclohexene

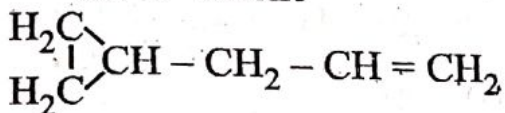
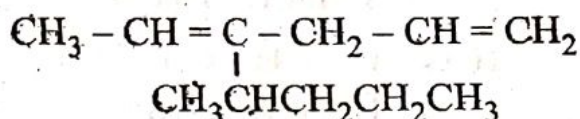
$$CH_3-\underset{H}{C}=\underset{H}{C}-CH_3$$

cis -2- butene

$$CH_3CH_2(H)C=C(H)(CH_2I)$$

trans-1-Iodo-2-pentene

$$H_2C, H_2C \text{ (ring) } CH-CH_2-CH=CH_2$$

3-Cyclopropyl-1- propene

$$CH_3-CH=\underset{CH_3CHCH_2CH_2CH_3}{C}-CH_2-CH=CH_2$$

4-(1-Methylbutyl)-1,4- hexadiene

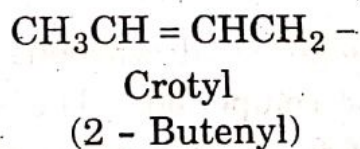
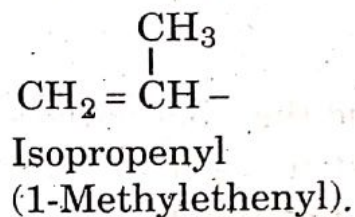
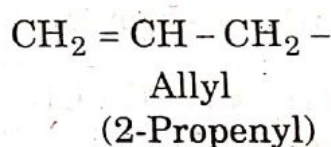
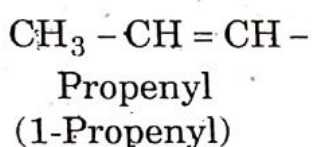
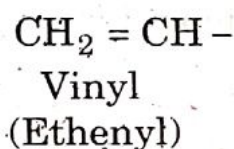
There are a few important alkenyl groups for which trivial (common) names are used preferentially in place of systematic names. These are

$CH_2=CH-$ Vinyl (Ethenyl)

$CH_3-CH=CH-$ Propenyl (1-Propenyl)

$CH_2=CH-CH_2-$ Allyl (2-Propenyl)

$CH_2=\underset{CH_3}{C}H-$ Isopropenyl (1-Methylethenyl).

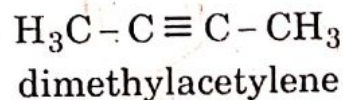
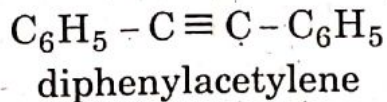
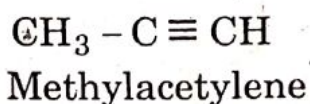
$CH_3CH=CHCH_2-$ Crotyl (2 - Butenyl)

4. Alkynes

Hydrocarbons that contain a carbon – carbon triple bond are called alkynes. The simplest alkyne, $HC\equiv CH$ is commonly called **acetylene**.

The simple alkynes are named in the common system as derivatives of acetylene.

$CH_3-C\equiv CH$ Methylacetylene

$C_6H_5-C\equiv C-C_6H_5$ diphenylacetylene

$H_3C-C\equiv C-CH_3$ dimethylacetylene

The IUPAC rules for naming alkynes are analogous to those for alkenes.

(i) Select the longest continuous carbon chain containing the triple bond as the parent chain which is then named by replacing the ending –ane of the corresponding alkane by –yne.

(ii) Number the parent chain from the end nearer to the triple bond.

(iii) Indicate the position of the triple bond by putting the number of lower numbered carbon of the triple bond before the name of the alkyne.

(iv) Alkyl groups and other substituents are numbered, named and placed as prefixes in alphabetic order.

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(v) Alkynes containing two triple bonds are named as **alkadiynes**.

(vi) If both double and triple bonds are present in a molecule, the double bond takes precedence over the triple bond, then the hydrocarbon is named as an alkenyne, alkadienyne, alkendiyne, etc., depending on the number of double and triple bonds in the molecule. The numbers to the multiple bonds are assigned in such a way that the total of the number remain as low as possible.

$$^{5}CH_3-{}^{4}CH_2-{}^{3}CH(CH_3)-{}^{2}C\equiv{}^{1}CH$$

3-Methyl-1-pentyne

$$CH_3-CH(CH_3)-C\equiv C-C(CH_3)_2-CH_3$$

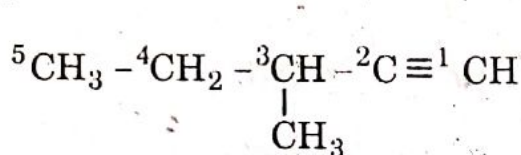
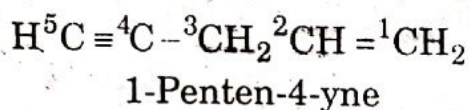
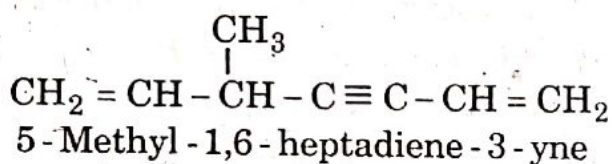
2,2,5- Trimethyl-3-hexyne

$$H^{5}C\equiv{}^{4}C-{}^{3}CH_2{}^{2}CH={}^{1}CH_2$$

1-Penten-4-yne

$$CH_3CH=CH-C\equiv C-C\equiv CH$$

5-Hepten-1,3-diyne

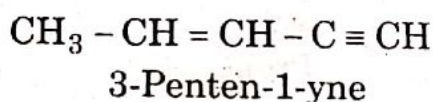
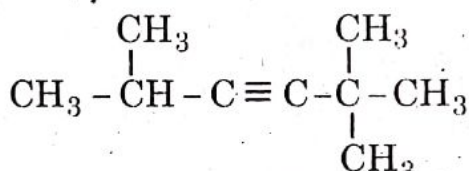
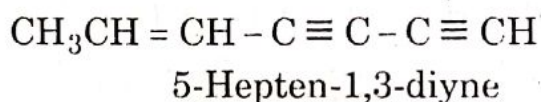
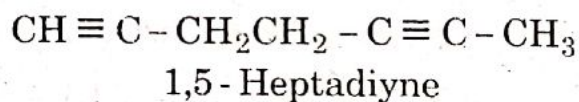
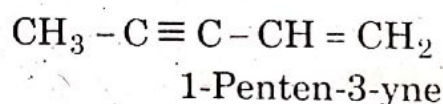
$$CH_2=CH-CH(CH_3)-C\equiv C-CH=CH_2$$

5-Methyl-1,6-heptadiene-3-yne

$$CH\equiv C-CH_2CH_2-C\equiv C-CH_3$$

1,5-Heptadiyne

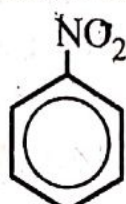
$$CH_3-CH=CH-C\equiv CH$$

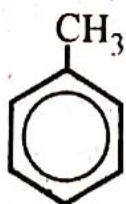
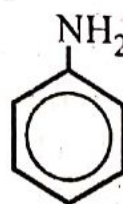
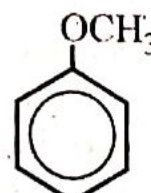
3-Penten-1-yne

$$CH_3-C\equiv C-CH=CH_2$$

1-Penten-3-yne

5. Aromatic Hydrocarbons

The nomenclature of the aromatic hydrocarbons and their derivatives is more complex than that of the aliphatic compounds. The system used for naming the benzene derivatives generally depends on the number of substituents on the benzene ring.

1. Monosubstituted benzene derivatives are systematically named as one word by combining the name of the substituent as a prefix with the word benzene, e.g.,

Ethylbenzene Nitrobenzene Bromobenzene

A number of monosubstituted benzene derivatives have common names which are currently accepted. The IUPAC names are given in brackets.

Toluene (Methylbenzene) Phenol (Hydroxybenzene) Aniline (Aminobenzene) Anisole (Methoxybenzene)

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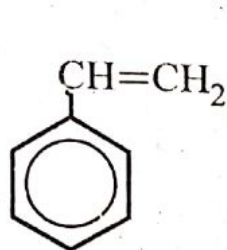
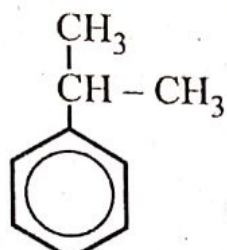
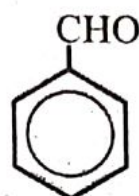
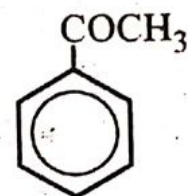
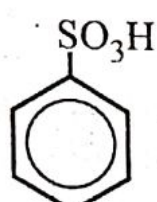
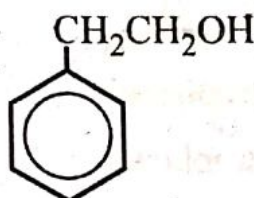
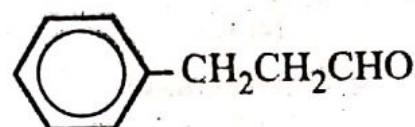
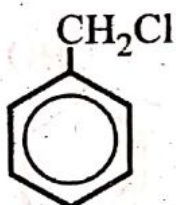
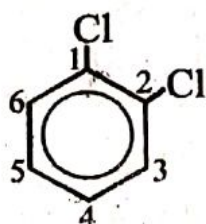
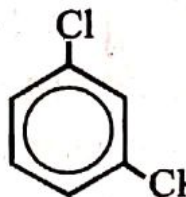

Styrene (Phenylethylene) — Cumene (Isopropylbenzene) — Benzaldehyde — Acetophenone

Benzoic acid — Benzenesulphonic acid

Sometimes, it is more convenient to name the benzene ring as a substituent, the phenyl group, C_6H_5

Phenylacetylene — 2-Phenylethanol — 3-Phenylpropanal

Another common aromatic substituent is Benzyl group which is abbreviated as $C_6H_5CH_2-$.

Benzyl chloride — Benzyl

2. In disubstituted benzene derivatives, the relative positions of the substituents in the benzene ring are indicated by the numbers allocated to the carbon atoms of the ring to which the substituents are attached or by using the prefixes ortho *(o-)*, *meta (m-)*, and *para (p-)* for the 1,2-, 1,3-, and 1,4- substituents, respectively. For example,

1,2-Dichlorobenzene or *o*-Dichlorobenzene — 1,3-Dichlorobenzene or *m*-Dichlorobenzene — 1,4-Dichlorobenzene or *p*-Dichlorobenzene

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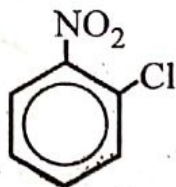
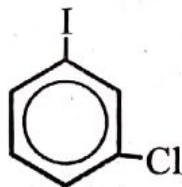
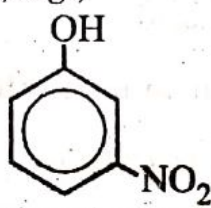
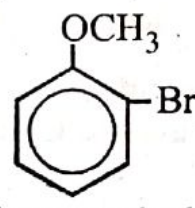
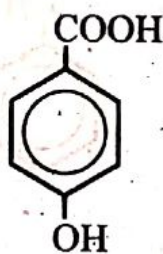
If the two substituents are different, both are used as prefixes successively in alphabetic order. The whole name is used in one word.

NO_2, Cl — 2-Chloronitrobenzene or *o*-Chloronitrobenzene

I, Cl — 3-Chloroiodobenzene or *m*-Chloroiodobenzene

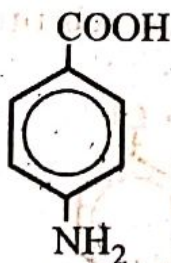
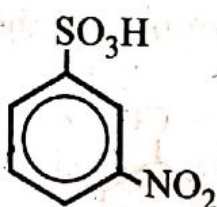
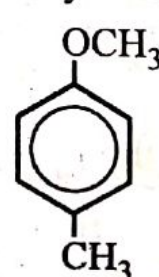
NO_2, Br — 4-Bromonitrobenzene or *p*-Bromonitrobenzene

If one of the substituents is such that it gives a special name to the molecule, then the special name is used as the parent name, the disubstituted compound is named as a derivative of that parent, e.g.,

4-Nitrotoluene or ***p*-Nitrotoluene**

3-Nitrophenol or ***m*-Nitrophenol**

2-bromoanisole or ***o*-bromoanisole**

If both substituents are such that they independently give a special name to the molecule, then the substituent which is normally treated as suffix gives the parent name to the molecule.

4-Aminophenol or ***p*-Aminophenol**

4-Hydroxybenzoic acid ***p*-Hydroxybenzoic acid**

4-Methoxybenzaldehyde or ***p*-Methoxybenzaldehyde**

4-Aminobenzoic acid or *p*-Aminobenzoic acid

3-Nitrobenzenesulphonic acid or *m*-Nitrobenzenesulphonic acid

p-methylanisole

Some disubstituted benzene derivatives also have special names that represent the benzene ring together with both the substituents, e.g.,

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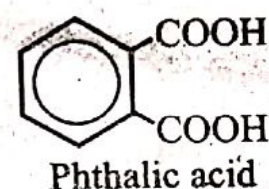
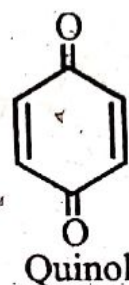
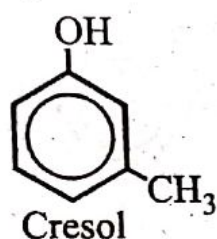
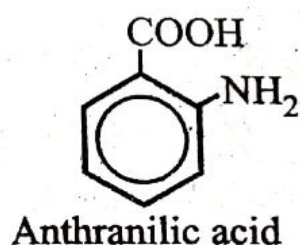
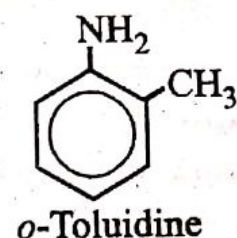
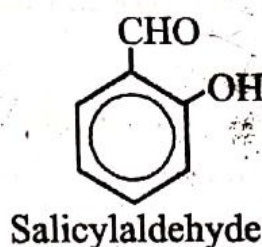
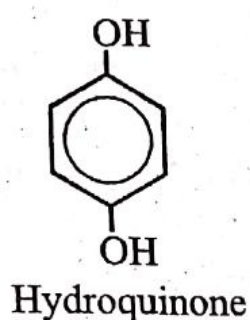
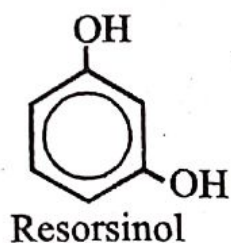
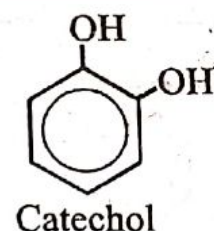
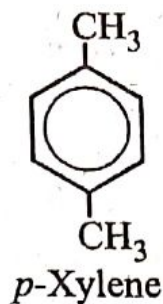
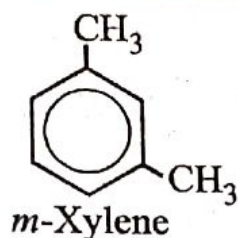
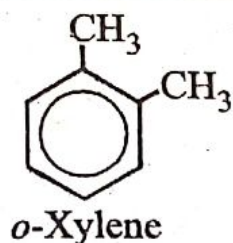
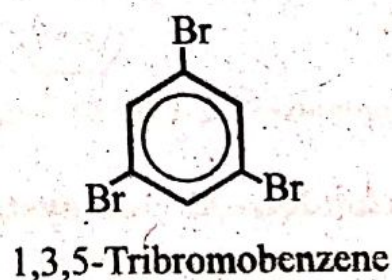
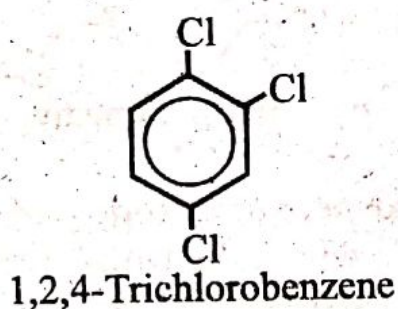
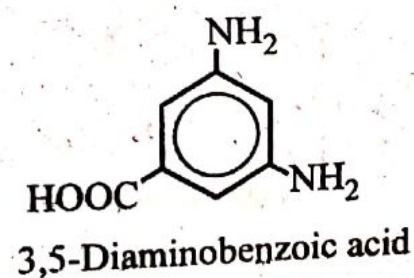
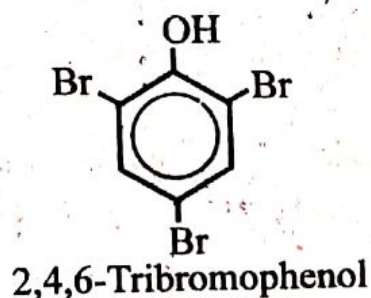
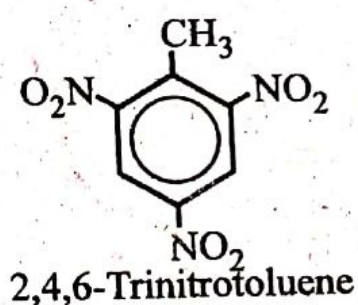
o-Xylene *m*-Xylene *p*-Xylene Catechol

Resorsinol Hydroquinone Salicylaldehyde *o*-Toluidine

Anthranilic acid Cresol Quinol Phthalic acid

Polysubstituted Benzenes. When three or more substituents are attached to the benzene ring, numbers must be used to designate their positions. If all the substituents are the same, the benzene ring is numbered so as to give the lowest total of the numbers assigned to the substituents, e.g.,

1,2,4-Trichlorobenzene 1,3,5-Tribromobenzene

If one of the substituents gives a special name to the molecule, then only the remaining positions of substituents are mentioned.

2,4,6-Trinitrotoluene 2,4,6-Tribromophenol 3,5-Diaminobenzoic acid

Some Polysubstituted benzene derivatives also have special names.

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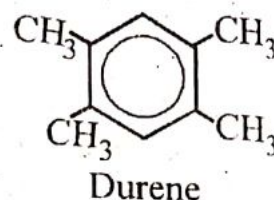
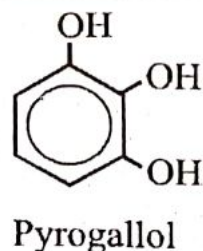
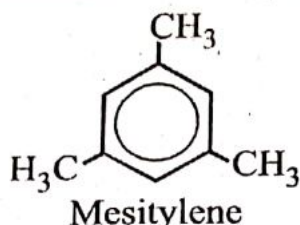
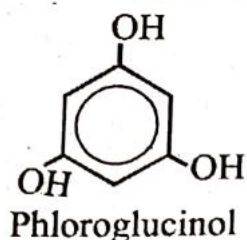
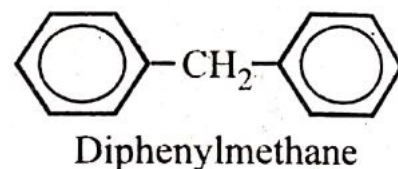
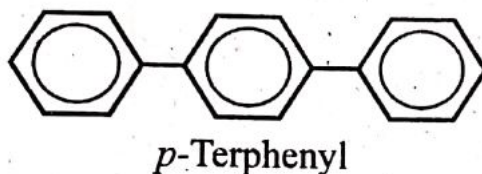
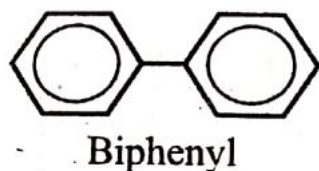
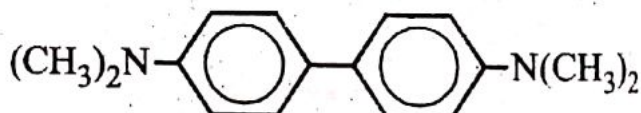
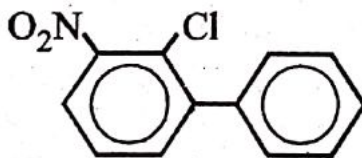
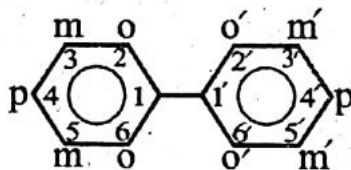
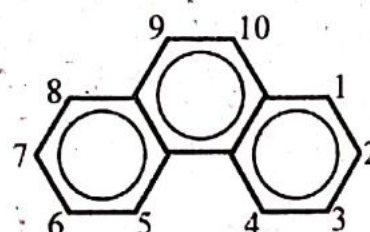
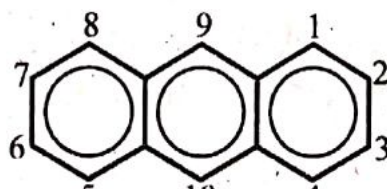
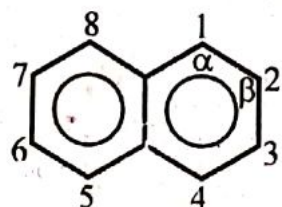
Phloroglucinol Mesitylene Pyrogallol Durene

Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic compounds have **more than one** benzene ring. **Biphenyl**, $C_6H_5-C_6H_5$, and **triphenylmethane**, $(C_6H_5)_3CH$, have **isolated rings**. Benzene rings sharing 2 ortho carbons' are **fused** or **condensed ring system**.

Isolated ring systems. The following are the important compounds of isolated ring systems.

Biphenyl p-Terphenyl Diphenylmethane

The numbering system in biphenyl is:

3-Chlorobiphenyl 2-Chloro-3-nitrobiphenyl *p,p′*-di(N,N-dimethylamino)biphenyl

Fused or Condensed ring systems. Naphthalene, anthracene and phenanthrene are the most important members of this class, in which the benzene rings are fused together at ortho positions so that the adjacent rings have a common carbon-carbon bond.

Naphthalene Anthracene Phenanthrene

In the IUPAC system of nomenclature, numbers are assigned only to those positions of the fused ring aromatic hydrocarbons at which substitution can take place as shown in the above structures.

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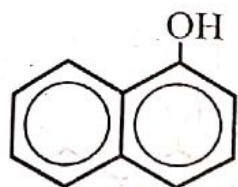
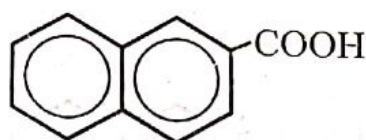
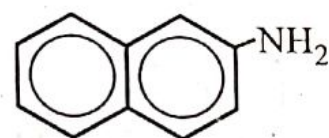
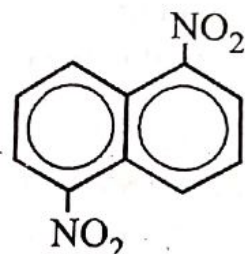
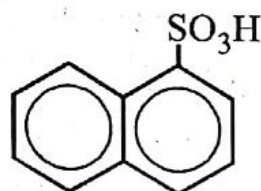
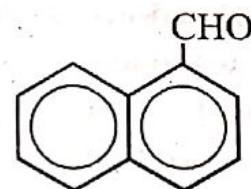
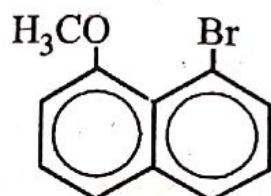
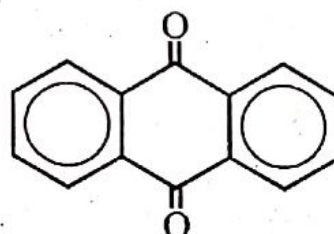
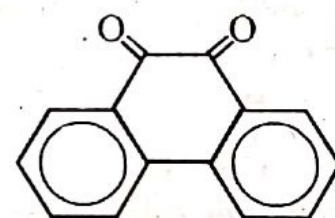
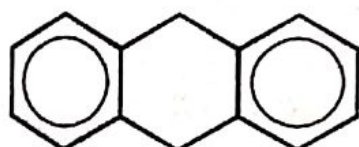
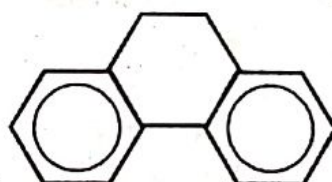
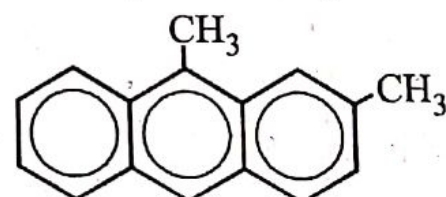
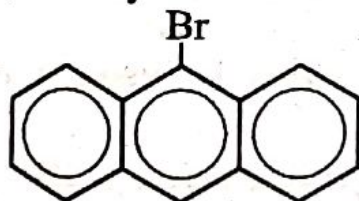
The substituted naphthalene derivatives are usually designated by the prefixes α– and β–. The numbering system begins with number 1 at the α– position.

6. Alkyl Halides

Monohaloalkanes are usually called **alkyl halides** and they contain carbon-halogen bonds. They are classified as primary, secondary, or tertiary, depending upon whether the halogen atom is bonded to a primary, secondary, or tertiary carbon atom. Abbreviations for these terms are 1°, 2°, and 3° respectively.

The common names of alkyl halides are obtained by naming the alkyl group attached to the halogen and adding the name of halide corresponding to halogen as a separate word.

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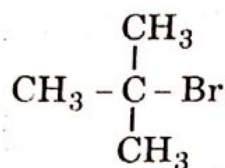
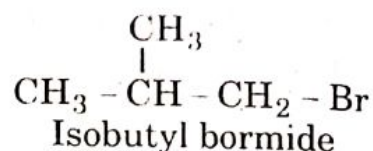
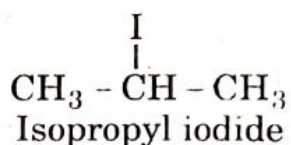
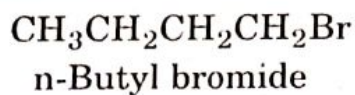
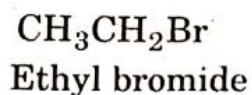
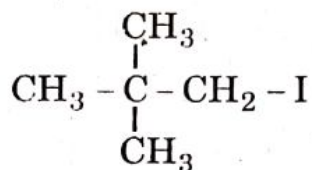
CH_3CH_2Br
Ethyl bromide

$CH_3CH_2CH_2CH_2Br$
n-Butyl bromide

$CH_3-CH(I)-CH_3$
Isopropyl iodide

$CH_3-CH(CH_3)-CH_2-Br$
Isobutyl bormide

$CH_3-C(CH_3)_2-Br$
tert. Butyl bromide

$CH_3-C(CH_3)_2-CH_2-I$
Neopentyl iodide

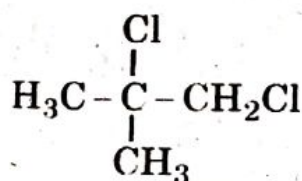
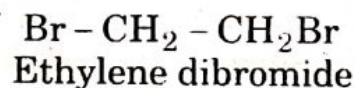
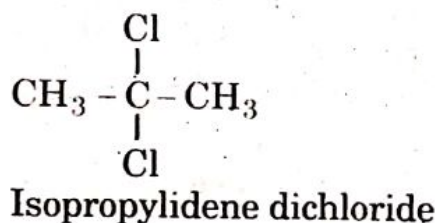
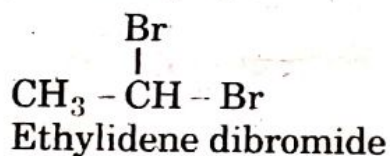
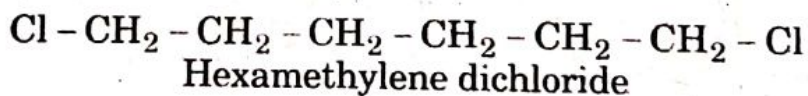
Dihaloalkanes are named according to the relative positions of the halogen atoms. If two halogen atoms are attached to the same carbon atom, i.e. in the *germinal* (*gem-*) position, it is named as an *alkylidene dihalide*. If the two halogen atoms are on adjacent carbon atoms, i.e., in the *vicinal* (*vic-*) position, it is named as a dihalide of the alkene from which it may be prepared by the addition of halogen. If the halogen atoms are on the terminal carbon atoms of the chain it is named as the polymethylene dihalide.

For example,

$CH_3-CH(Br)-Br$
Ethylidene dibromide

$CH_3-C(Cl)_2-CH_3$
Isopropylidene dichloride

$Br-CH_2-CH_2Br$
Ethylene dibromide

$H_3C-C(Cl)(CH_3)-CH_2Cl$
Isobutene dichloride

$Cl-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-Cl$
Hexamethylene dichloride

IUPAC System: The IUPAC names of alkyl halides are obtained by using the following rules:

1. Select the longest chain to which the halogen is attached and give it the name of the corresponding alkanes.
2. Prefix the name of alkane by halo; i.e., chloro, bromo, iodo or fluoro.
3. Number the chain so as to give the carbon carrying the halogen atom the lowest possible number.
4. Other substituents are numbered, named and placed as prefixes in alphabetic order. For example

$CH_3-CH(Br)-CH_3$
2 – Bromopropane

$CH_3-CH_2-CH(CH_3)-CH_2Cl$
1 - Chloro - 2 - methylbutane

$CH_3-C(Br)(CH_3)CH_2-Br$
1,2 - Dibromo - 2 - methylpropane

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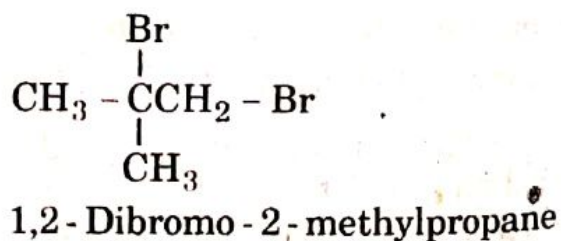
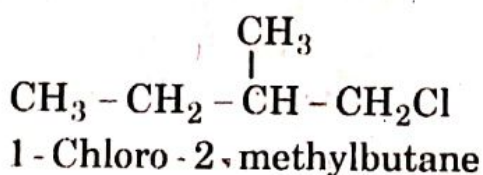
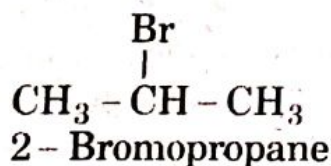
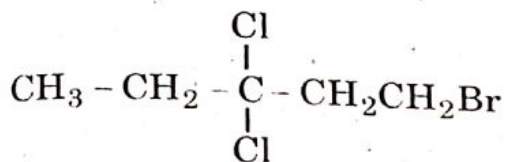
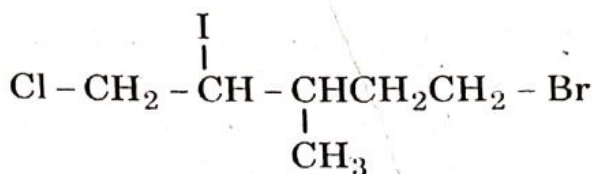
$$CH_3-CH_2-\underset{Cl}{\overset{Cl}{C}}-CH_2CH_2Br$$

1-Bromo-3,3-dichloropentane

$$Cl-CH_2-\overset{I}{CH}-\underset{CH_3}{CH}CH_2CH_2-Br$$

5-Bromo-1-chloro-2-iodo-3-methylpentane

7. Organometallic Compounds

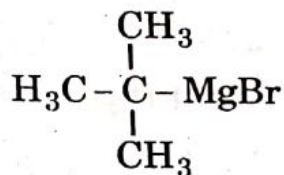
Organometallic compounds are named as **alkylmetals.**

CH_3CH_2Li
Ethyllithium

$(CH_3CH_2)_4Pb$
Tetraethyllead

If the metal is bonded to an inorganic anion as well as a carbon atom, the compounds is named as a derivative of the inorganic salt.

CH_3CH_2MgBr
Ethylmagnesium bromide

$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-MgBr$$

tert-butylmagnesium bromide

8. Alcohols

Common System: In this system alcohols (R–OH) are named by naming the alkyl group attached to the –OH group and adding alcohol as a separate word.

$CH_3CH_2CH_2OH$
n-propyl alcohol

$$\overset{CH_3}{CH_3CHOH}$$

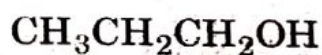
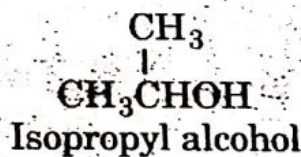
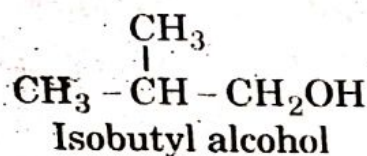
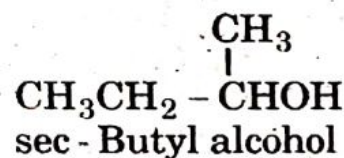
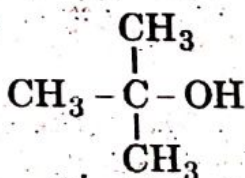
Isopropyl alcohol

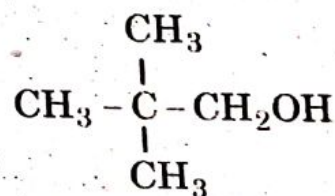
$$CH_3-\overset{CH_3}{CH}-CH_2OH$$

Isobutyl alcohol

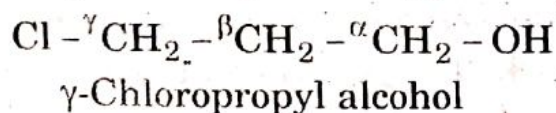
$$CH_3CH_2-\overset{CH_3}{CHOH}$$

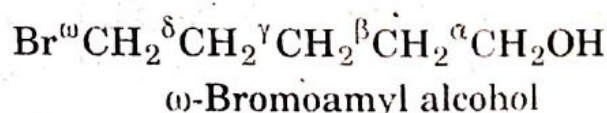
sec-Butyl alcohol

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

tert-Butyl alcohol

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH$$

Neopentyl alcohol

The positions of the other substituents in the alkyl groups are indicated by the Greek letters α(alpha), β(beta), γ(gamma), and δ(delta). The carbon atom bearing the hydroxyl group is named as α, next carbon atoms named as β,γ,δ and so on respectively.

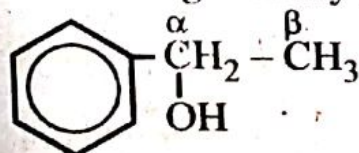
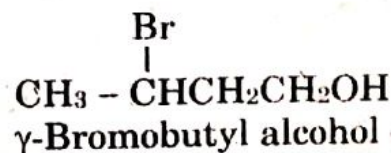
$$Cl-{}^{\gamma}CH_2-{}^{\beta}CH_2-{}^{\alpha}CH_2-OH$$

γ-Chloropropyl alcohol

$$Br{}^{\omega}CH_2{}^{\delta}CH_2{}^{\gamma}CH_2{}^{\beta}CH_2{}^{\alpha}CH_2OH$$

ω-Bromoamyl alcohol

An alcohol, $C_5H_{11}OH$ containing five carbons is commonly called amyl alcohol and the end carbon is generally named as ω(omega).

$$C_6H_5-\underset{OH}{\overset{\alpha}{C}H_2}-\overset{\beta}{C}H_3$$

α-phenylethyl alcohol

$$CH_3-\overset{Br}{CH}CH_2CH_2OH$$

γ-Bromobutyl alcohol

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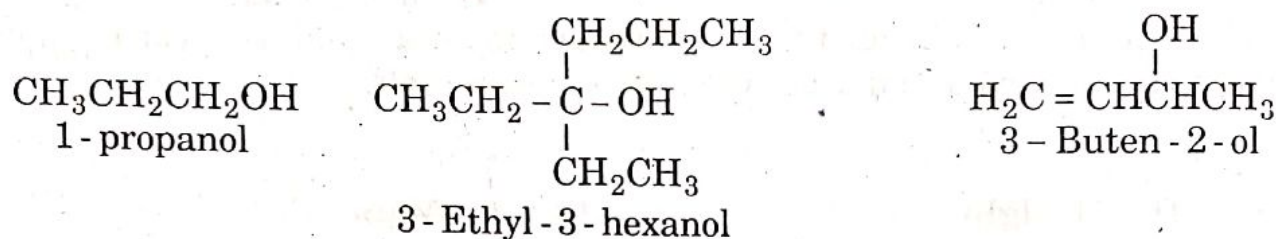
IUPAC System: 1.Select the longest carbon chain containing the hydroxyl group as the parent alkane.

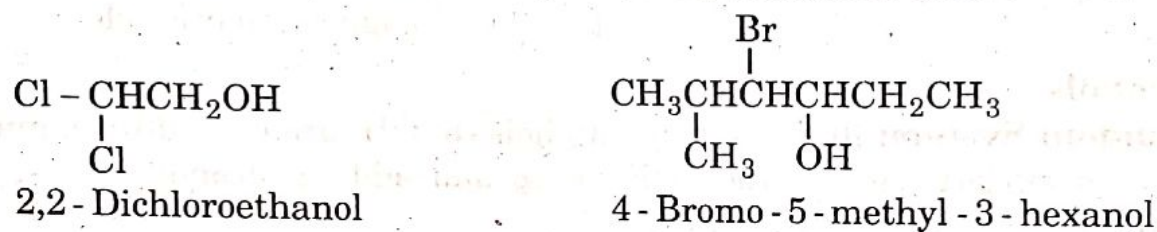
2. The name is obtained by replacing the ending -e of the name of the parent alkane by -ol. Thus, the alcohols are named as alkanols.
3. The position of the hydroxyl group is indicated by the number of the carbon attached to the -OH group, and is written before the name of the alkanol.
4. Other substituents are numbered, named and placed as prefixes in alphabetic order.

$CH_3CH_2CH_2OH$
1 - propanol

$CH_3CH_2-C(CH_2CH_2CH_3)(CH_2CH_3)-OH$
3 - Ethyl - 3 - hexanol

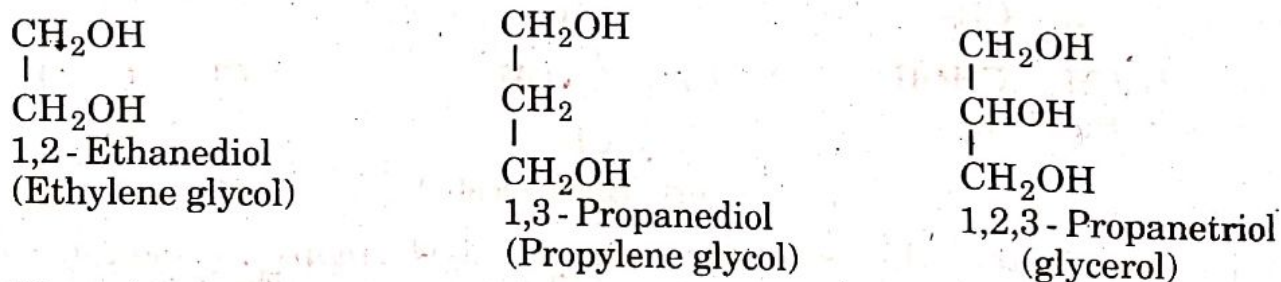
$H_2C=CHCH(OH)CH_3$
3 – Buten - 2 - ol

Note that in IUPAC system the OH is given a lower number than C = C or Cl.

$Cl-CH(Cl)CH_2OH$
2,2 - Dichloroethanol

$CH_3CH(CH_3)CH(Br)CH(OH)CH_2CH_3$
4 - Bromo - 5 - methyl - 3 - hexanol

Diols and Triols have both common and IUPAC names. The IUPAC names are obtained by adding the suffix diol or triol to the name of the parent alkane containing two or three –OH groups respectively. The positions of the –OH groups are indicated by the numbers. For example

CH_2OH-CH_2OH
1,2 - Ethanediol
(Ethylene glycol)

$CH_2OH-CH_2-CH_2OH$
1,3 - Propanediol
(Propylene glycol)

$CH_2OH-CHOH-CH_2OH$
1,2,3 - Propanetriol
(glycerol)

9. Phenols

Compounds containing an –OH group attached directly to an aromatic ring are called **Phenols**. Phenols are usually named by common system or as derivatives of the parent phenol, C_6H_5OH which is called hydroxybenzene. Their systematic names are also given in parentheses.

Phenol (Hydroxybenzene)
o-Cresol (2-Methylphenol)
p-Nitrophenol (4-Nitrophenol)

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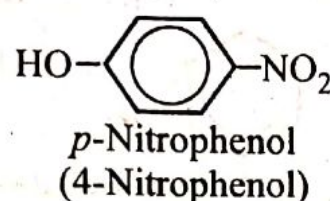
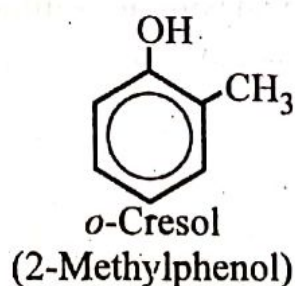
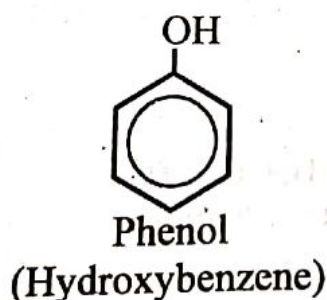
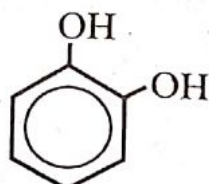
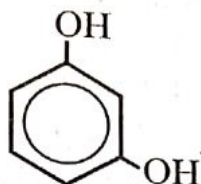
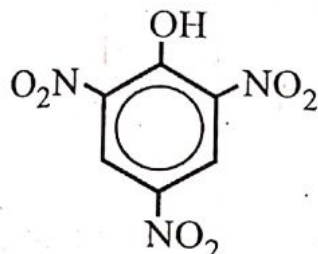
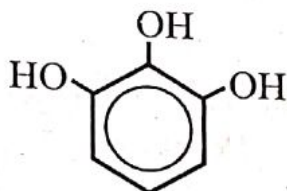
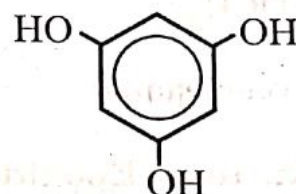
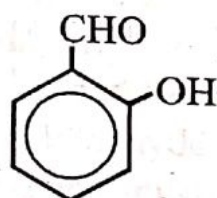
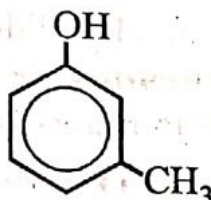
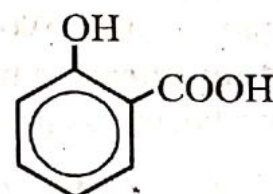
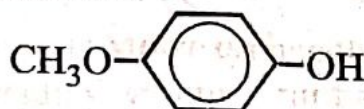
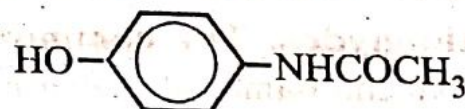
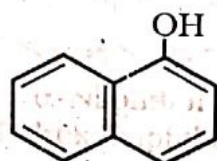
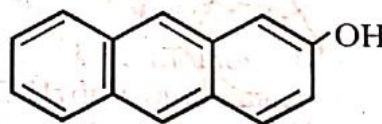
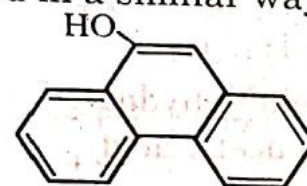

Catechol
(o-Dihydroxybenzene)

Resorcinol
(m-Dihydroxybenzene)

Hydroquinone
(p-Dihydroxybenzene)

Picric acid
(2,4,6-Trinitrophenol)

Pyrogallol
(1,2,3-Hydroxybenzene)

Phyloroglucinol
(1,3,5-Trihydroxybenzene)

Salicylaldehyde
(o-hydroxybenzaldehyde)

m-Cresol
(m-hydroxytoluene)

Salicylic acid
(o-Hydroxybenzoic acid)

While naming the polyfunctional aromatic compounds, the hydroxy function is usually placed low in order precedence; only the amino and the ether functions are placed lower than the hydroxy function.

p-hydroxybenzoic acid

p-Methoxyphenol

p-Hydroxyacetanilide

Compounds with the hydroxyl group attached to a polycyclic benzenoid ring system also belong to the phenol faimly and they are named in a similar ways;

α-Naphthol
(1-Hydroxynaphthalene)

2-Anthranol
(2-Hydroxyanthrancene)

9-Phenanthrol
(9-Hydroxyphenanthrene)

10. Ethers

Common system. In the common system, the names of ethers are derived by naming the two alkyl groups attached to the oxygen atom, in alphabetic order, followed by the word ether. If the groups are same, the prefix di- is used with the group.

$C_2H_5OC_2H_5$
Diethyl ether

$CH_3CH_2OCH_3$
Ethyl methyl ether

$(CH_3)_2CHOC_2H_5$
Isopropyl ethyl ether

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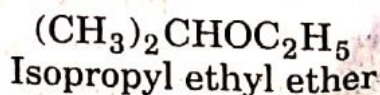
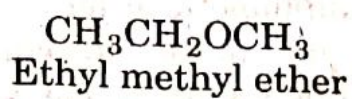
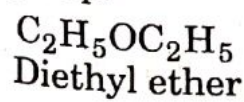
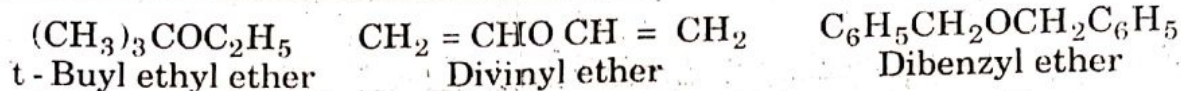
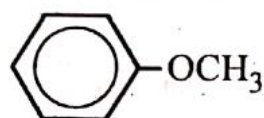
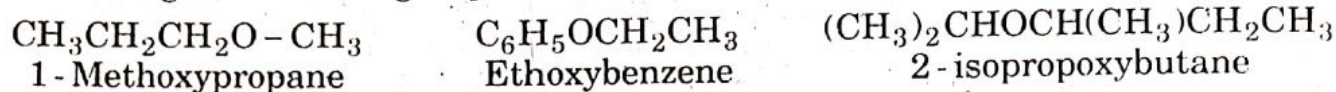
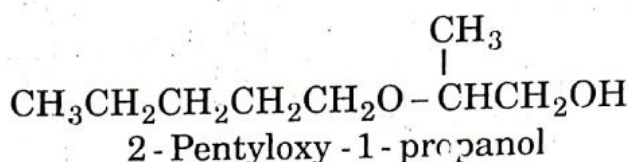
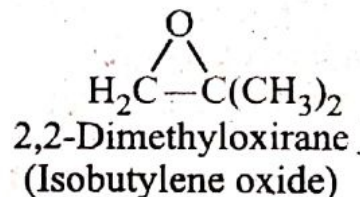
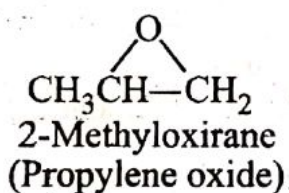
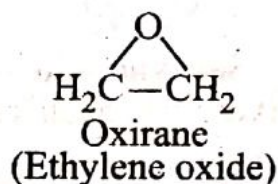
$(CH_3)_3COC_2H_5$ t - Buyl ethyl ether | $CH_2 = CHO\,CH = CH_2$ Divinyl ether | $C_6H_5CH_2OCH_2C_6H_5$ Dibenzyl ether

In the **IUPAC system**, ethers are named as **Alkoxyalkanes** or compounds containing a functional group of higher priority than ether.

$CH_3CH_2CH_2O-CH_3$ 1 - Methoxypropane | $C_6H_5OCH_2CH_3$ Ethoxybenzene | $(CH_3)_2CHOCH(CH_3)CH_2CH_3$ 2 - isopropoxybutane

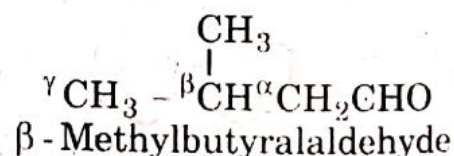
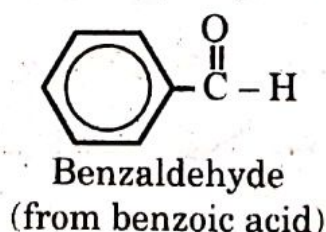
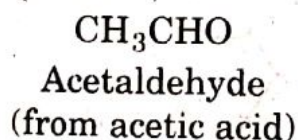
Methoxycyclohexane

$CH_3CH_2CH_2CH_2CH_2O-CH(CH_3)CH_2OH$
2 - Pentyloxy - 1 - propanol

11. Oxiranes (Epoxides)

Oxiranes are cyclic ethers in which the ether oxygen is part of the three membered ring. Oxiranes are also called *epoxides*. Because they are readily prepared from alkenes, they are commonly known as *alkene oxides*. In the **IUPAC system**, they are named as **alkyloxiranes**. Substituents on the oxirane ring require a numbering system. The oxygen atom is given the number 1.

H_2C-CH_2 (bridged by O) Oxirane (Ethylene oxide) | CH_3CH-CH_2 (bridged by O) 2-Methyloxirane (Propylene oxide) | $H_2C-C(CH_3)_2$ (bridged by O) 2,2-Dimethyloxirane (Isobutylene oxide)

12. Aldehydes and Ketones

Aldehydes. The common name. The common names of aldehydes are derived from the names of the corresponding acids by replacing the suffix **-ic** (or -oic) acid by aldehyde. Locations of substituent groups are designated by Greek letters α-, β-, γ- and so on, beginning with the carbon next to carbonyl group.

CH_3CHO Acetaldehyde (from acetic acid) | $C_6H_5-C(=O)-H$ Benzaldehyde (from benzoic acid) | ${}^{\gamma}CH_3-{}^{\beta}CH(CH_3){}^{\alpha}CH_2CHO$ β - Methylbutyralaldehyde

IUPAC System. In the IUPAC system, aldehydes are named as **alkanals**.

Select the longest chain containing the aldehyde group and replace the final **-e** from the name of the corresponding alkane by the suffix -al. The C of CHO is number 1. Since the aldehyde group is always at the end of the chain, there is no need to indicate its position. However, the positions of the substituents are indicated by number, named and placed as prefixes in alphabetic order.

When there are two aldehyde groups in a molecules it is named as **Alkanedial**. Notice that -e of the corresponding alkane name is retained.

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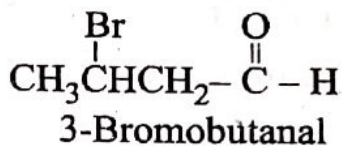
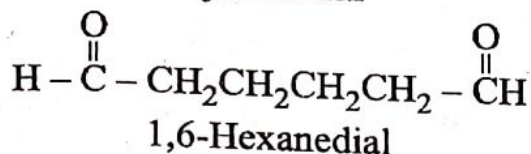
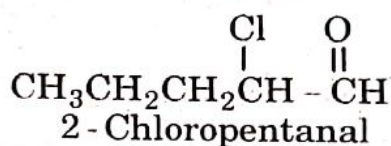
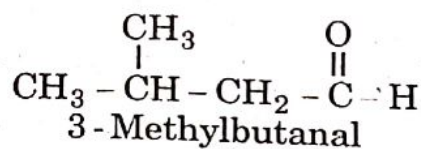
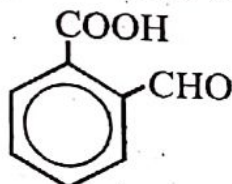
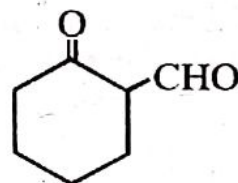
$CH_3-\underset{}{CH}(CH_3)-CH_2-\overset{O}{\overset{\|}{C}}-H$
3-Methylbutanal

$CH_3CH_2CH_2\overset{Cl}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}H}$
2-Chloropentanal

$H-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}H}$
1,6-Hexanedial

$CH_3\overset{Br}{\overset{|}{C}H}CH_2-\overset{O}{\overset{\|}{C}}-H$
3-Bromobutanal

When –CHO group is used as substituent, it is named as a formyl group.

o-Formylbenzoic acid

2-Formylcyclohexanone

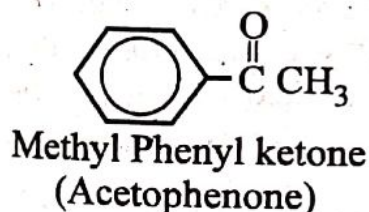
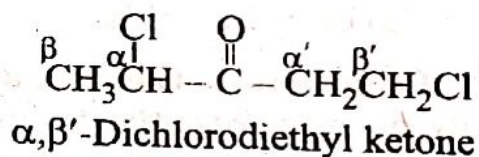
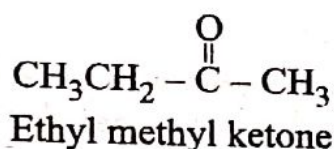
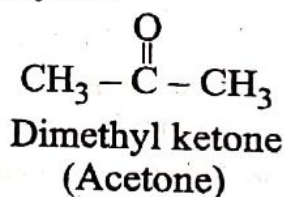
Ketones. Common name. The common names of ketones are obtained by naming the alkyl groups attached to the carbonyl group separately in alphabetical order and adding the word ketone. For symmetrical ketones the prefix di- is used. The positions of the substituents are indicated by the Greek letters as in the case of aldehydes.

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$
Dimethyl ketone
(Acetone)

$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3$
Ethyl methyl ketone

$\overset{\beta}{C}H_3\overset{\alpha}{\overset{Cl}{\overset{|}{C}H}}-\overset{O}{\overset{\|}{C}}-\overset{\alpha'}{C}H_2\overset{\beta'}{C}H_2Cl$
α,β′-Dichlorodiethyl ketone

$C_6H_5-\overset{O}{\overset{\|}{C}}\ CH_3$
Methyl Phenyl ketone
(Acetophenone)

$C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$
Diphenyl ketone
(Benzophenone)

The ketones in which the carbonyl group is attached to a benzene ring, are named as –phenone, as shown above in parentheses.

In the **IUPAC System** the names of ketones are derived from the names of the corresponding alkanes by replacing the ending –e with –one. The position of the keto group is indicated by numbering the parent chain from one end so that the carbonyl group gets the lowest possible number. The substituents are numbered, named and placed as prefixes in alphabetic order.

When there are two carbonyl groups in a molecule, it is named as **Alkanedione**

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3$
Butanone

$CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-CH_3$
3-Methyl-2-butanone

$H_2C=CHCOCH_3$
3-Buten-2-one

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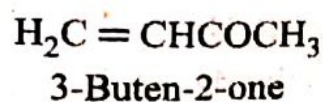
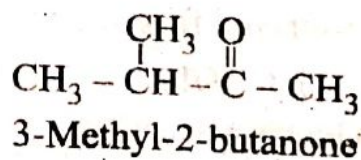
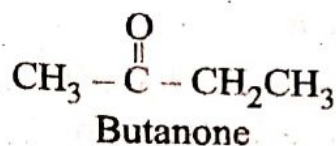
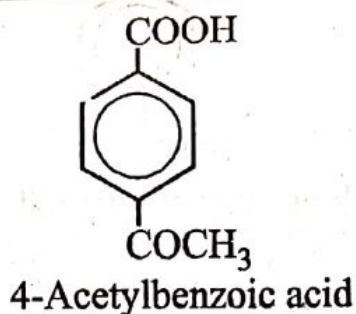
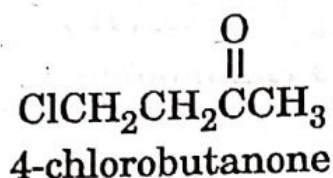
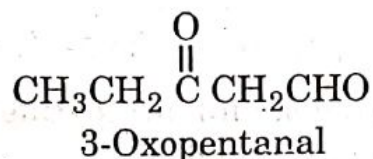

Sometimes a carbonyl compound also contains a more important functional group. In such cases, the prefix **oxo-**, along with a number indicating its position in the chain, is used for the carbonyl group.

$$CH_3CH_2\overset{\overset{O}{\parallel}}{C}CH_2CHO$$

3-Oxopentanal

The general order of precedence of the functional group in naming the compound is: acid anhydride > carboxylic acid > sulphonic acid > ester > acid halide > amide > aldehyde > ketone > alcohol ≈ phenol > ether > amine

The C=O group has numbering priority over the C=C group.

13. Carboxylic acids

Common or trivial names. The common names of the carboxylic acids are usually derived from the Latin or Greek words that indicate one of their original source. All common names of acids end in –ic acid. Common names, such as formic (ant) and **butyric** (butter) acids, are based on the natural source of the acid. The positions of substituetnt groups are shown by Greek letters α, β, γ, δ, etc. The carbon atom adjacent to the carboxyl carbon is assigned the letter α , the next carbon on the chain β, the next one γ, and so on. Some common names of carboxylic acids are given below:

CH_3COOH	CH_3CH_2COOH	$CH_3CH_2CH_2COOH$
acetic acid	Propionic acid	Butyric acid
$CH_3(CH_2)_4COOH$	$(CH_3)_3CCOOH$	$(GH_3)_2{}^{\gamma}CH^{\beta}CH_2{}^{\alpha}CH_2COOH$
Caproic acid	Pivalic acid	γ-methylvaleric acid
$CH_3(CH_2)_3COOH$	$CH_3(CH_2)_{14}COOH$	$CH_3(CH_2)_{16}COOH$
Valeric acid	Palmitic acid	Stearic acid
C_6H_5COOH	$o-HOC_6H_4COOH$	$C_6H_5{}^{\gamma}CH_2{}^{\beta}CH_2{}^{\alpha}CH_2COOH$
Benzoic acid	Salicylic acid	γ-Phenylbutyric acid
$C_{10}H_7COOH$	$CH_3(CH_2)_8COOH$	$(CH_3)_2C(OH)COOH$
Naphthoic acid	Capric acid	α-Hydroxyisobutyric acid

Some carboxylic acids have names derived from acetic acids, e.g.

$(CH_3)_3COOH$	$C_6H_5CH_2COOH$	$(CH_3)_2CHCH_2COOH$
Trimethylacetic acid	Phenyl acetic acid	Isopropylacetic acid

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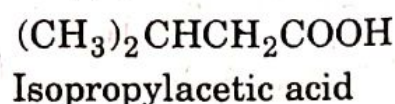
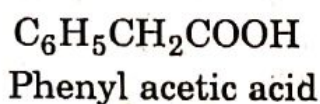
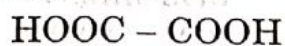
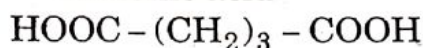
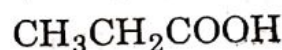
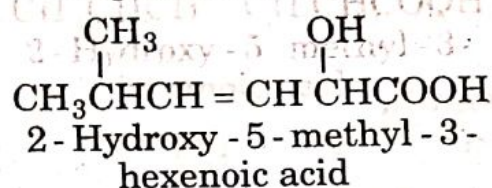
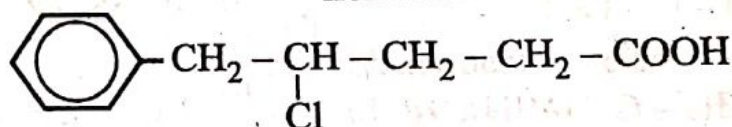

The four simplest of the dicarboxylic acids are known exclusively by their common names.

$HOOC-COOH$	$HOOC-CH_2COOH$
Oxalic acid	Malonic acid
$HOOC-(CH_2)_2COOH$	$HOOC-(CH_2)_3-COOH$
Succinic acid	Glutaric acid

IUPAC System. In the IUPAC system, the name of the carboxylic acid is obtained from the chain of carboxylic acid, by replacing the ending -e of the corresponding alkane by **–oic acid**. The positions of the substituents are indicated by numbers. The carboxyl carbon is always given number 1, the carbon adjacent to it is given the number 2, and so on.

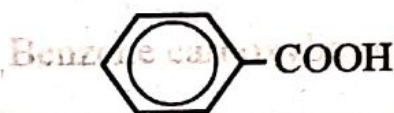
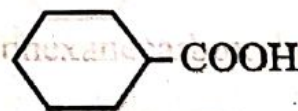
$HCOOH$
Methanoic acid

CH_3COOH
Ethanoic acid

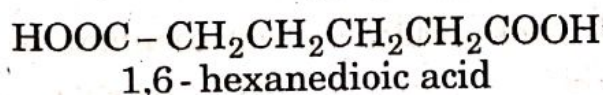
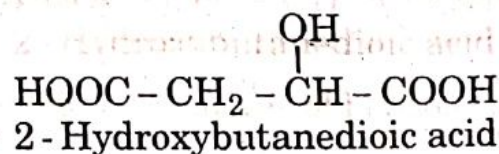
CH_3CH_2COOH
Propanoic acid

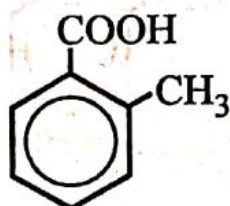
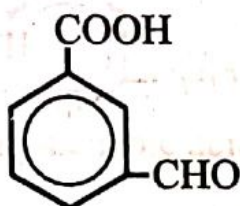
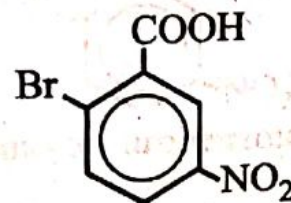
$CH_3CH_2CH_2COOH$
Butanoic acid

$CH_3-CH(Br)-COOH$
2 - Bromopropanoic acid

$CH_3CH(CH_3)CH=CHCH(OH)COOH$
2 - Hydroxy - 5 - methyl - 3 - hexenoic acid

$CH_3C\equiv CCH_2CH_2COOH$
4-Hexynoic acid

$C_6H_5-CH_2-CH(Cl)-CH_2-CH_2-COOH$
4-chloro-5-phenylpentanoic acid

It is not convenient to name a cyclic carboxylic acid by IUPAC system, however, occasionally they are named as carboxylic acids, e.g.

C_6H_5-COOH
Benzene carboxylic acid

$C_6H_{11}-COOH$
Cyclohexanecarboxylic acid

The common names acceptable in the IUPAC system are acetic acid and benzoic acid, although most of the common names are still in use.

Dicarboxylic acids are named by adding the suffix **–dioic** and the word **acid** to the longest chain with the two COOH's.

$HOOC-CH_2CH_2CH_2CH_2COOH$
1,6 - hexanedioic acid

$HOOC-CH_2-CH(OH)-COOH$
2 - Hydroxybutanedioic acid

Aromatic carboxylic acids are usually named as derivatives of benzoic acid, e.g.

o-$CH_3C_6H_4COOH$
o-**Methylbenzoic acid**

m-**Formylbenzoic acid**

2-Bromo-5-nitrobenzoic acid

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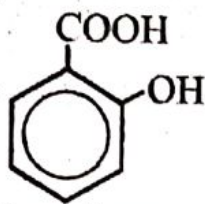
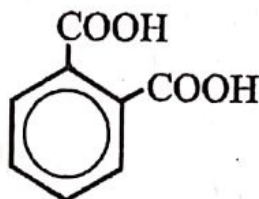
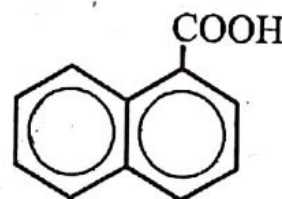
The names of some important acids are given below. Their common names are given in parentheses.

2-Hydroxybenzene carboxylic acid (Salicylic acid)	Benzene-1,2-dicarboxylic acid (Phthalic acid)	Naphthalene-1-carboxylic acid (α-Naphthoic acid)

Derivatives of Carboxylic Acids

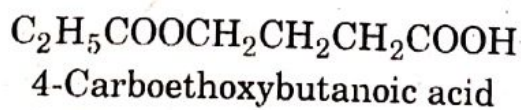
14. Esters

The names of esters are derived by writing the name of alkyl group of the alcohol, followed by the name of the acid with the ending **–ic** acid replaced by **–ate**. This nomenclature applies to both common and IUPAC names of esters.

Formula	Common Name	IUPAC Name
$H-\overset{O}{\overset{\|}{C}}-OCH_3$	Methyl formate	Methyl methanoate
$CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$	Ethyl acetate	Ethyl ethanoate
$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$	Methyl butyrate	Methyl butanoate
$CH_3-\overset{CH_3}{\overset{\mid}{CH}}-\overset{O}{\overset{\|}{C}}-OCH_3$	Methyl isobutyrate	Methyl isobutanoate

If the ester function (–COOR) is to be treated as a substituent, it is treated as a **carboalkoxy** group.

$$C_2H_5COOCH_2CH_2CH_2COOH$$

4-Carboethoxybutanoic acid

15. Acid Halides

Acid halides are the derivatives of carboxylic acids in which the -OH of carboxyl group has been replaced by a halogen atom.

Acid halides are named in both the common and IUPAC systems by dropping the ending 'ic acid' from the name of the parent acid and adding the suffix '-yl halide'.

Formula	Common Name	IUPAC Name
CH_3COCl	Acetyl chloride	Ethanoyl chloride
CH_3CH_2COCl	Propionyl chloride	Propanoyl chloride
$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl$	Benzoyl chloride	

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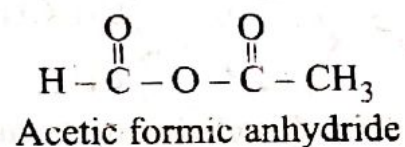
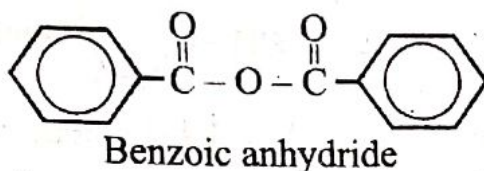
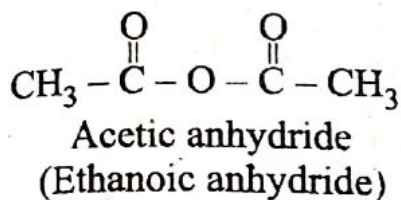
16. Acid Anhydrides

Acid anhydrides are the compounds which are obtained after the elimination of a water molecule from the carboxyl groups of two carboxylic acid molecules (or from the two carboxyl groups of dicarboxylic acids).

Acid anhydrides are named by replacing the word 'acid' in the name of parent acid by 'anhydride'. For mixed acid anhydrides, the parent name of each acid is written in alphabetical order, followed by the word anhydride.

$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$
Acetic anhydride
(Ethanoic anhydride)

$C_6H_5-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5$
Benzoic anhydride

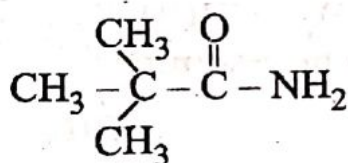
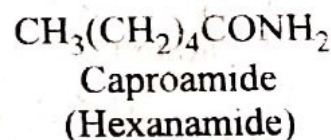
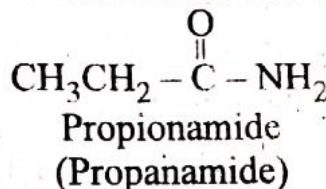
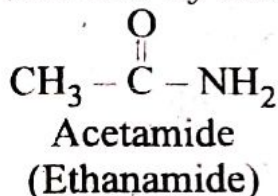
$H-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$
Acetic formic anhydride

17. Amides

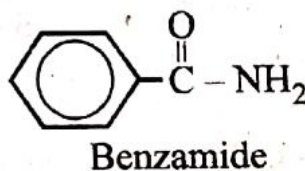
Amides are the compounds in which -OH of the carboxyl group has been replaced by an amino group, $-NH_2$.

Simple amides are named by replacing the ending '-ic acid' (Common) or -oic acid (IUPAC) by the word 'amide'. The IUPAC names are given in parentheses.

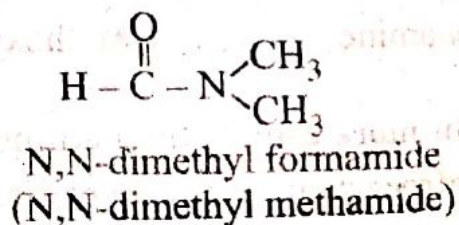
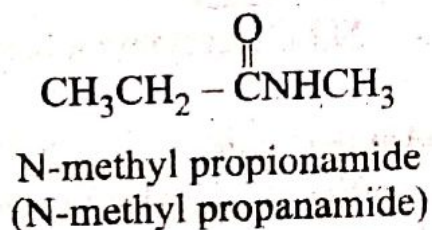
$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$
Acetamide
(Ethanamide)

$CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2$
Propionamide
(Propanamide)

$CH_3(CH_2)_4CONH_2$
Caproamide
(Hexanamide)

$CH_3-C(CH_3)_2-\overset{O}{\overset{\|}{C}}-NH_2$
2,2-dimethylpropionamide
(2,2-dimethyl propanamide)

$C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2$
Benzamide

When nitrogen is substituted, this is indicated by prefixing the name of a simple amide by N-, followed by the name of the substituent group. This method is used for both systems of nomenclature.

$CH_3CH_2-\overset{O}{\overset{\|}{C}}NHCH_3$
N-methyl propionamide
(N-methyl propanamide)

$H-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$
N,N-dimethyl formamide
(N,N-dimethyl methamide)

18. Amines

Common Names. The common names of amines are derived by using the suffix -amine, preceded by the name or names of the alkyl groups attached to the nitrogen atom, in alphabetical order. The prefixes di- or tri- are used for identical alkyl groups. The name is written as one word.

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CH_3NH_2
Methylamine

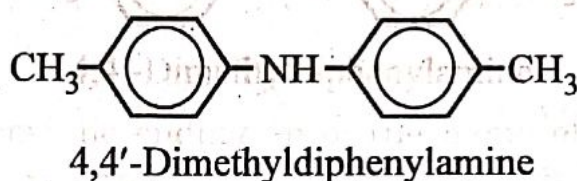
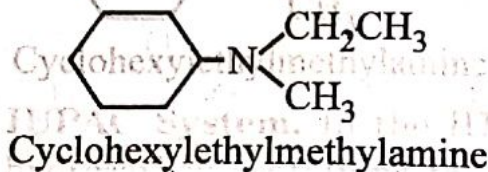
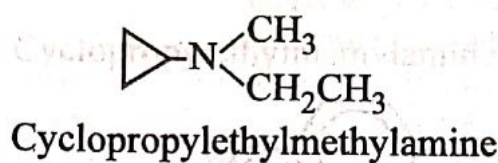
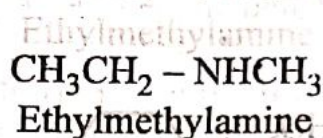
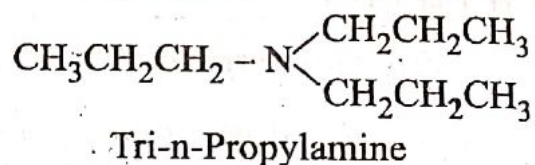
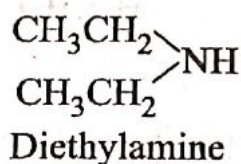
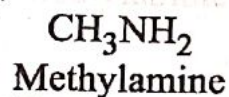
$CH_3CH_2 \backslash NH / CH_3CH_2$
Diethylamine

$CH_3CH_2CH_2-N(CH_2CH_2CH_3)_2$
Tri-n-Propylamine

$CH_3CH_2-NHCH_3$
Ethylmethylamine

$C_3H_5-N(CH_3)(CH_2CH_3)$
Cyclopropylethylmethylamine

$C_6H_{11}-N(CH_2CH_3)(CH_3)$
Cyclohexylethylmethylamine

$CH_3-C_6H_4-NH-C_6H_4-CH_3$
4,4′-Dimethyldiphenylamine

IUPAC System. In the IUPAC system, the ending –e of the name of the parent hydrocarbon containing the $-NH_2$ group, is replaced by –amine. For secondary and tertiary amines, the longest chain is selected as the parent alkane; in case of equal chain -lengths the parent alkane is the one with the greater number of substituents. The remaining alkyl groups are named as substituents by using the prefix N- to indicate that they are attached to nitrogen.

$CH_3CH_2NH_2$
Ethanamine

$CH_3CH_2CH_2NH_2$
Propanamine

$(CH_3CH_2)_2NH$
N-Ethylethanamine

$(CH_3CH_2)_3N$
N,N - Diethylethanamine

$CH_3-CH(CH_3)-CH_2-CH(NH_2)CH_2CH_3$
5 - Methyl - 3 - hexanamine

$CH_3-CH(CH_3)-N(CH_2CH_3)-CH(NH_2)-CH_3$
N - ethyl - N - isopropyl - 1 - methylethanamine

$CH_3CH_2CH_2-NH-CH_2-CH(CH_3)-CH_3$
2 - Methyl - N - propylpropanamine

$C_6H_5-NH_2$
Benzenamine

$CH_3O-C_6H_4-NH_2$
4-Methoxybenzenamine

$C_6H_{11}-N(CH_2CH_3)-CH_2CH_3$
N,N-Diethylcyclohexanamine

In more complicated amines, the $-NH_2$ group is considered as a substituent on a hydrocarbon, and its position on the chain is indicated by the lowest possible number.

$CH_3-CH_2-CH(NH_2)-CH_2-CH(CH_3)-CH_3$
5 - Methyl - 3 - aminohexane

$CH_3-CH(NH_2)-COOH$
2-Aminopropanoic acid

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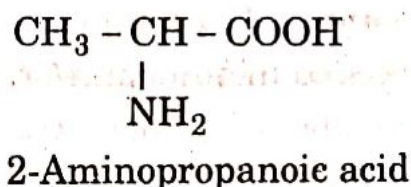
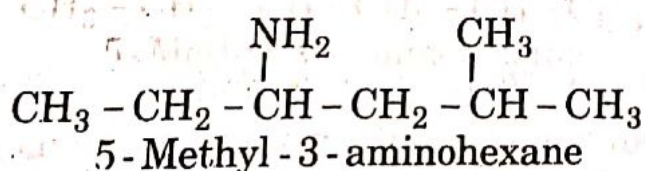
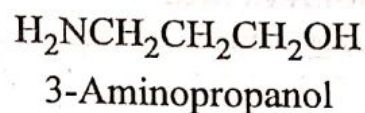
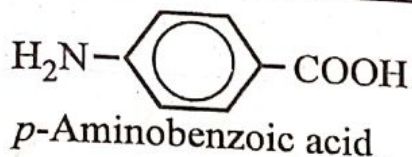
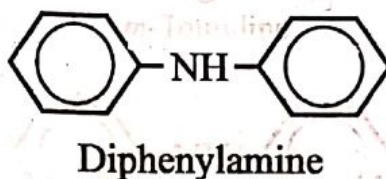
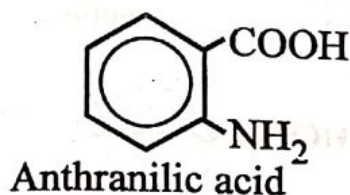
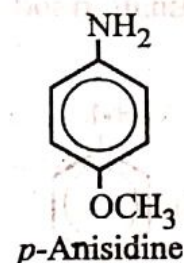
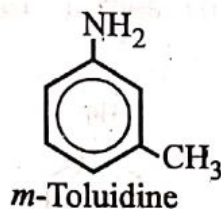
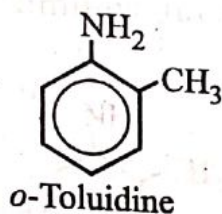
$H_2N-C_6H_4-COOH$

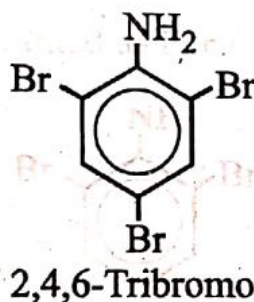
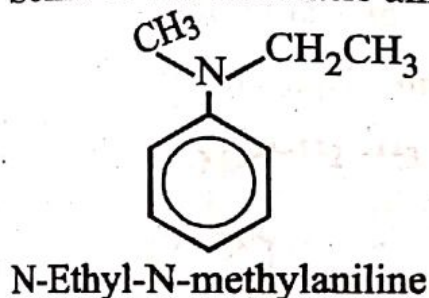
p-Aminobenzoic acid

$H_2NCH_2CH_2CH_2OH$

3-Aminopropanol

A number of aromatic amines have special names that have been accepted by IUPAC.

Aniline | *o*-Toluidine | *m*-Toluidine | *p*-Anisidine

Anthranilic acid | Diphenylamine

Some of the aromatic amines are named as derivatives of aniline.

N-Ethyl-N-methylaniline | 2,4,6-Tribromoaniline | *o*-Nitroaniline

3.3 Nomenclature of Polyfunctional Compounds

The functional group present in a compound determines its class. When a compound contains two or more different types of functional groups (polyfunctional compound), the functional group which specifies its class is the **principal functional group.** The other functional groups are considered as substituents. For example, the compounds $HOCH_2CH_2COCH_3$ must be named 4-hydroxy-2-butanone, not 4-butanol-2-one. The name 3-oxo-1- butanol is not preferred because the C=O group is the principal functional group as it ranks higher in the priority table.

Selection of the Principal Functional Group

The IUPAC system has established the priority of functional groups for determining the class of a polyfunctional compound. Table 3.2 gives a list of functional groups in decreasing order of priority for citation as the principal functional group. That is, the functional group which occurs higher up in the priority table is the principal functional group and specifies the class. Therefore, by having a look at the priority table, one can at once know the class of a polyfunctional structure

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Table 3.2 Nomenclature Priority for Determining the Principal Functional Group. Higher Priority Group is at the Top

Class	Functional group	Suffix used
Carboxylic acid	$-C(=O)-OH$	–oic acid
Sulphonic acid	$-SO_3H$	–sulphonic acid
Ester	$-C(=O)-O-$	Alkyl –oate
Acid halide	$-C(=O)-X$	–oyl halide
Amide	$-C(=O)-NH_2$	–amide
Nitrile	$-CN$	–nitrile
Aldehyde	$-C(=O)-H$	–al
Ketone	$-C(=O)-$	–one
Alcohol	$-OH$	–ol
Amine	$-N<$	Amine
Ethers	$-O-$	(ether)
Alkene	$>C=C<$	–ene
Alkyne	$-C\equiv C-$	–yne

Table 3.3 Prefixes used for Functional Groups

–Br	Bromo	–R	Alkyl	$-C(=O)-$	Oxo
–Cl	Chloro	–OR	Alkoxy	$-NO_2$	Nitro
–F	Fluoro	–OH	Hydroxy	–NO	Nitroso
–I	Iodo	$-NH_2$	Amino	–CN	Cyano

IUPAC Rules for Naming Polyfunctional Compounds

1. Identify the principal functional group and this gives the class name of the structure.
2. Number the longest chain containing the principal functional group from the end nearer to it.
3. Write the parent name corresponding to the number of carbons in the longest chain.
4. Arrange the substituent names with position numbers in alphabetical order.

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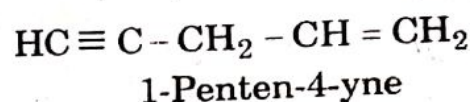
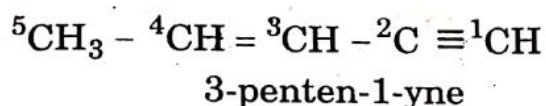
5. Prefix substituent names with the parent name.
6. The following functional groups are always named as substituents.

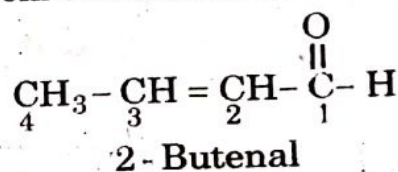
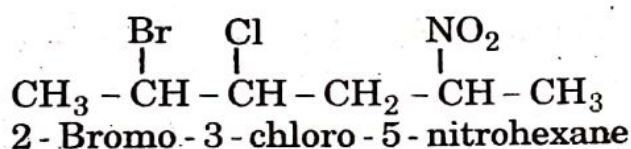
–Cl	Chloro	–R	Alkyl	$-NO_2$	Nitro
–Br	Bromo	–OR	Alkoxy	–NO	Nitroso
–I	Iodo	$-NH_2$	Amino		
–F	Fluoro	–CN	Cyano		

7. C–C double or triple bonds are usually indicated by integrating -en- or -yne- into the suffix.
8. Compounds containing a double bond (C=C) and a triple bond (C≡C) in the main chain are named as alkenynes. Their position number of the double bond is inserted before -alken- and that of triple bond before –yne.

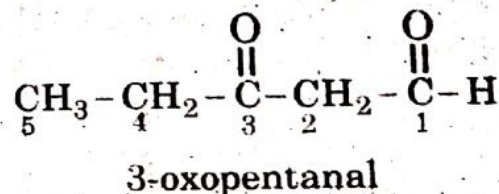
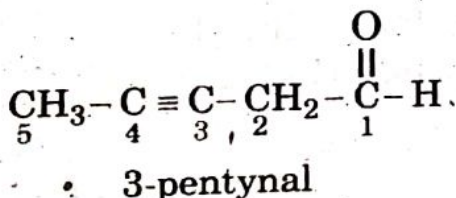
$^5CH_3-{}^4CH={}^3CH-{}^2C\equiv{}^1CH$
3-penten-1-yne

$HC\equiv C-CH_2-CH=CH_2$
1-Penten-4-yne

Remember that when a double bond and a triple bond can be given the same position number, the chain is numbered from the end closer to double bond.

$CH_3-CH(Br)-CH(Cl)-CH_2-CH(NO_2)-CH_3$
2 - Bromo - 3 - chloro - 5 - nitrohexane

$\underset{4}{CH_3}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{C}(=O)-H$
2 - Butenal

Remember that the –CHO group is the principal functional group, as it ranks higher in the priority table than the C=C group. The position number of –CHO is not indicated before –al as it is always 1.

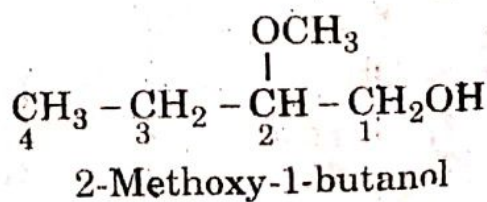
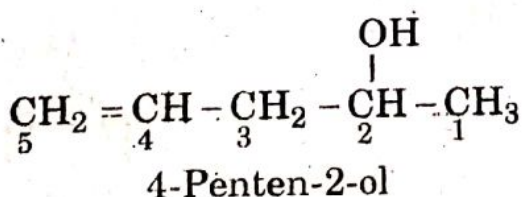
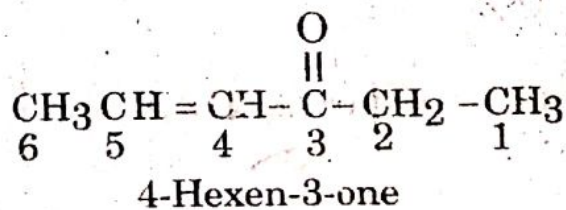
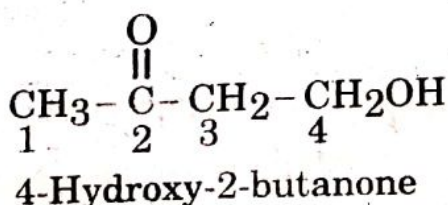
$\underset{5}{CH_3}-\underset{4}{C}\equiv\underset{3}{C}-\underset{2}{CH_2}-\underset{1}{C}(=O)-H$
3-pentynal

$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{C}(=O)-\underset{2}{CH_2}-\underset{1}{C}(=O)-H$
3-oxopentanal

Both C=O and –CHO form part of the longest chain. The –CHO group is the principal functional group as it ranks higher in the priority table. The ketonic carbonyl group, C=O, is indicated by the prefix oxo.

$\underset{1}{CH_3}-\underset{2}{C}(=O)-\underset{3}{CH_2}-\underset{4}{CH_2OH}$
4-Hydroxy-2-butanone

$\underset{6}{CH_3}\underset{5}{CH}=\underset{4}{CH}-\underset{3}{C}(=O)-\underset{2}{CH_2}-\underset{1}{CH_3}$
4-Hexen-3-one

$\underset{5}{CH_2}=\underset{4}{CH}-\underset{3}{CH_2}-\underset{2}{CH}(OH)-\underset{1}{CH_3}$
4-Penten-2-ol

$\underset{4}{CH_3}-\underset{3}{CH_2}-\underset{2}{CH}(OCH_3)-\underset{1}{CH_2OH}$
2-Methoxy-1-butanol

In both the above compounds, the –OH group is the principal functional groups. The $-OCH_3$ is always treated as a substituent and is indicated by the prefix methoxy.

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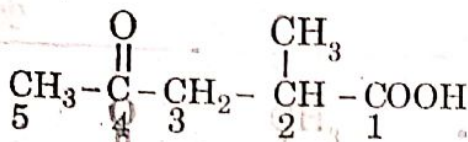
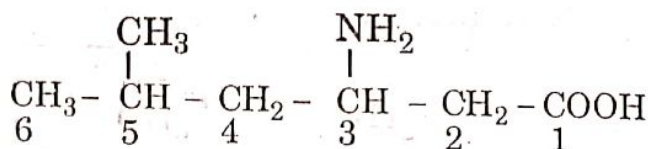
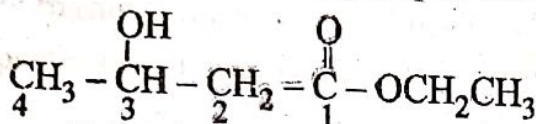
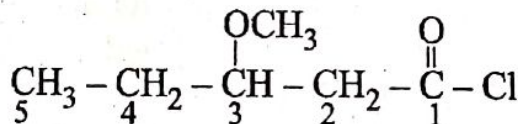
$$\overset{5}{CH_3}-\overset{4}{\underset{}{C}}(=O)-\overset{3}{CH_2}-\overset{2}{CH}(CH_3)-\overset{1}{COOH}$$

2–Methyl–4–oxopentanoic acid

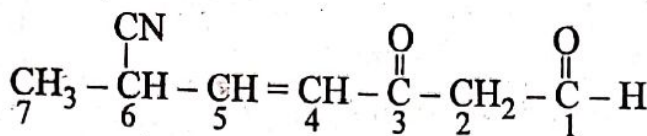
$$\overset{6}{CH_3}-\overset{5}{CH}(CH_3)-\overset{4}{CH_2}-\overset{3}{CH}(NH_2)-\overset{2}{CH_2}-\overset{1}{COOH}$$

3–Amino–5–methylhexanoic acid

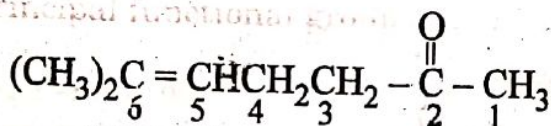
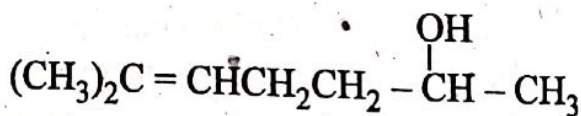
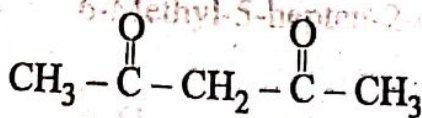
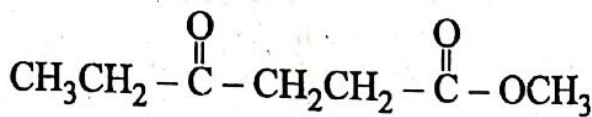
In both the above compounds, the –COOH groups is the funcational group as it ranks highest in the Priority table. The ketonic carbonyl group (C=O) is indicated by the prefix oxo. The $-NH_2$ group is indicated by the prefix amino.

$$\underset{4}{CH_3}-\underset{3}{CH}(OH)-\underset{2}{CH_2}-\underset{1}{C}(=O)-OCH_2CH_3$$

Ethyl-3-hydroxybutanoate

$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH}(OCH_3)-\underset{2}{CH_2}-\underset{1}{C}(=O)-Cl$$

3-Methoxypentanoyl chloride

The $-\overset{O}{\overset{\|}{C}}-O$ group is the principal functional group and the compound is named as ester. The $-\overset{O}{\overset{\|}{C}}-Cl$ is the principal functional group and the compound is named as an acid halide.

$$\underset{7}{CH_3}-\underset{6}{CH}(CN)-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{C}(=O)-\underset{2}{CH_2}-\underset{1}{C}(=O)-H$$

6-cyano-3-oxo-4-heptenal

The functional groups are –CN, C=C, –CO–, and –CHO. The –CHO group is the principal functional group and the compound is named as aldehyde.

$$(CH_3)_2\underset{6}{C}=\underset{5}{C}H\underset{4}{C}H_2\underset{3}{C}H_2-\underset{2}{C}(=O)-\underset{1}{CH_3}$$

6-Methyl-5-hepten-2-one

$$(CH_3)_2C=CHCH_2CH_2-CH(OH)-CH_3$$

6-Methyl-5-hepten-2-ol

$$CH_3-C(=O)-CH_2-C(=O)-CH_3$$

2,4-Pentanedione

$$CH_3CH_2-C(=O)-CH_2CH_2-C(=O)-OCH_3$$

Methyl-4-oxohexanoate

(benzene ring with COOH and OH)

o-Hydroxybenzoic acid (Salicylic acid)

(benzene ring with CH_2CH_3 and OCH_3 para)

p-Methoxyethylbenzene

(benzene ring with OH and $CH_2CH=CH_2$ para)

p-allylphenol

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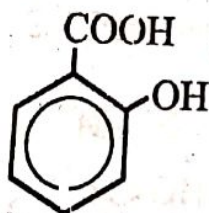
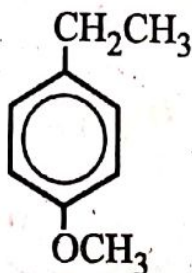
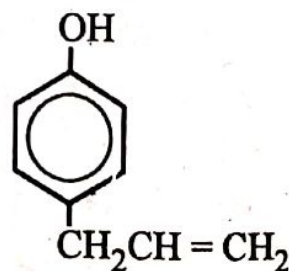
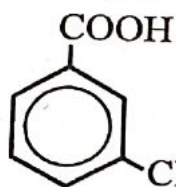
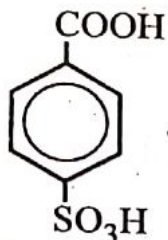
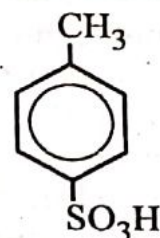

m-formylbenzoic acid *p*-sulphobenzoic acid *p*-Toluenesulphonic acid

3.4 Heterocyclic Compounds

Thos cyclic compounds which, in addition to carbon, have at least one atom of another element (heteroatom) in the ring are called **heterocyclic compounds** or simply **heterocycles**.

Common Names Heterocyclic compounds are usually called by their common names. Their numbering starts from the hetero atom and proceeds around the ring so as to give the substituents the lowest number.

IUPAC System. The system combines prefixes, which indicate the nature of the hetero atom present, with stems, which indicate the size of the ring. The prefixes are the same as those listed in table. 3.4 for use in substitution names, except the terminal a is usually elided since the stems, which are listed in table 3.5 all begin with vowels. When there is more than one kind of ring hetero atom, the atom of higher atomic number receives the lower number in naming the compound.

Table.3.4 Characteristic Prefixes for Replacement Names

Element	Prefix
Oxygen	oxa–
Nitrogen	aza–
Sulphur	Thia
Phosphorus	Phospha
Silicon	Sila

Table. 3.5. Stem for use in Nomenclature of Heterocyclic Compounds

Ring size	Stem	
	Saturated	Unsaturated
3	Irane	irine
4	etane	ete
5	olane	ole
6	ixane	ixine
7	epane	epine
8	ocanc	ocine

(i) In numbering rings, a single hetero atom is given number 1. The substituents are then numbered in the usual manner.

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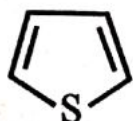
(ii) When a hetero atom occurs more than once, the hetero atoms are given the lowest possible numbers.

(iii) If isomers are possible as a result of the positions of one or more hydrogens, the position of each hydrogen is indicated by means of the prefix 1H, 2H, 3H etc.

The IUPAC names are given in parentheses.

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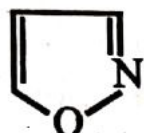
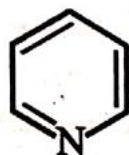
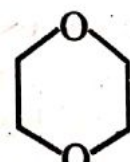
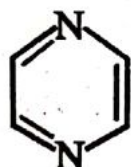
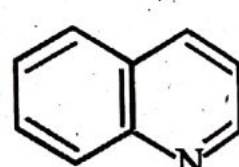
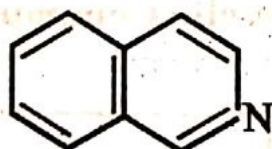
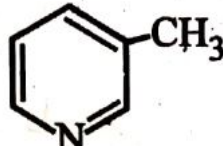
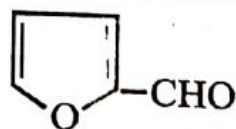
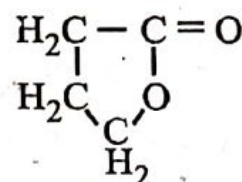
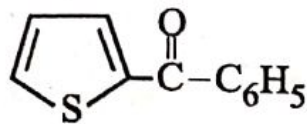
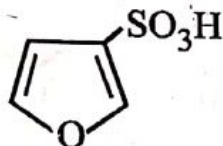
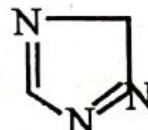
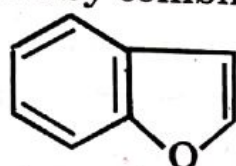
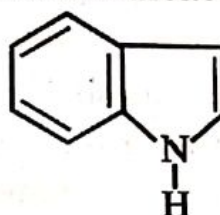
–CHO

Furfural
(2-formyloxole)

Isonicotinic acid
(azixine-4-carboxylic acid)

$H_2C - C = O$
$H_2C \quad O$
CH_2

γ-Butyrolactone
(oxalane-2-one)

$-\overset{O}{\overset{\|}{C}}-C_6H_5$

2-benzoylthiophene
2-benzoylthiole)

3-furansulphonic acid

(3H-1,2,4-triazole)

Heterocyclic compounds containing more than one ring are conveniently named by combining the names of the indicated rings, e.g.,

benzofuran

benzopyrrole

Questions

1. Name the following alkyl groups: (a) CH_3- (b) CH_3CH_2- (c) $CH_3CH_2CH_2-$ (d) $(CH_3)_2CH-$ (e) $(CH_3)_3C-$

2. Write the structural formulas for the following compounds:

(a)	2-Buten-1-ol	(b)	6-Methyl-5-hepten-2-ol
(c)	2-Pentanone	(d)	1,3-Butadiene
(e)	3-Hydroxypropanoic acid	(f)	4-penten-2-one
(g)	6-cyano-3-oxo-4-heptenal	(h)	4-oxopentanoic acid

3. Write structural formulas for the following compounds.

(a) p-Nitroaniline (b) Mesitylene (c) Durene
(d) Biphenyl (e) Cumene (f) Anthrancene
(g) Triphenylmethanol (h) 3-oxopentanal
(i) 4-Acetylbenzoic acid (j) Benzoic anhydride

4. Write the IUPAC names of the following compounds.

(a) $H-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$ (b) $HO-CH_2-CH_2-COOH$

(c) $CH_2=CH-C\equiv CH$ (d) $CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

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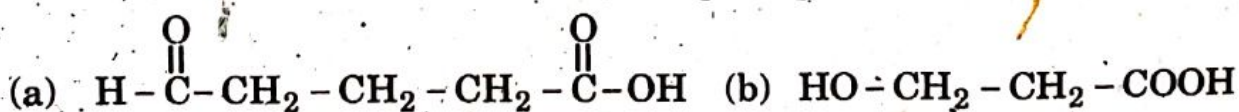
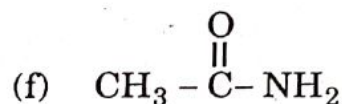
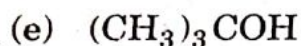
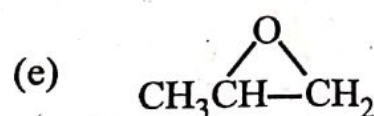
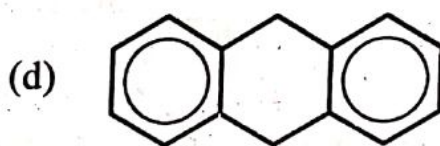
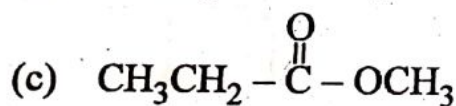
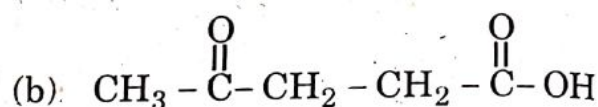
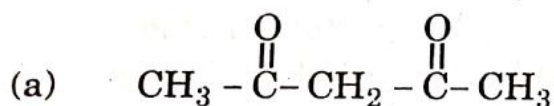
(e) $(CH_3)_3COH$ (f) $CH_3-\overset{\overset{\displaystyle O}{||}}{C}-NH_2$

5. Write the IUPAC names of the following compounds:

(a) $CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$

(b)

(c) $CH_3CH_2-\overset{\overset{\displaystyle O}{||}}{C}-OCH_3$ (d) (e)

(f) $HC\equiv CCH_2CH=CH_2$ (g)

6. Write the structure of the followings according to IUPAC system.
(i) Methyl isobutyl ketone (ii) Propionaldehyde diethyl acetal
(iii) Neopentyl alcohol (iv) *m*-Cresol (v) Stearic acid P.U. 1998

7.(a) Write the structural formulas of the following compounds
(i) 3-isobutyl -2,3 dimethyl pentane (ii) Optical active tartaric acid
(iii) 1-axial-3-equitorial- dimethyl cyclohexane (iv) N-Benzoylaniline
(v) Z-1-Bromo-1,2-dichloroethene

(b) Write the names of the following compounds according to the IUPAC system.

(i) H_2N-CH_2COOH (ii) $CH_3-\overset{+}{N}(CH_3)(C_2H_5)HCl^-$ (iii) $HC\equiv C-CH_2-C(CH_3)=CH_2$

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